

COMPOSITIONS, METHODS AND ARTICLES PRODUCED BY COMPOUNDING
POLYAMIDES WITH OLEFIN-MALEIC ANHYDRIDE POLYMERS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application claims priority under 35 U.S.C. § 119(e) to U.S. Provisional Application Serial Nos. 61/374,817, filed August 18, 2010; 61/485,826 filed May 13, 2011; and 61/493,058, filed June 3, 2011. The entirety of the disclosures of each of these applications are incorporated herein by reference

10 A polyamide is a polymer containing repeating units of amides. These polymers can occur both naturally, with examples being proteins, such as wool and silk, and can be made artificially through step-growth polymerization, with examples being nylons, aramids, and sodium poly(aspartate). Currently, polyamides are commonly used in textiles, automobiles, carpet and sportswear due to their extreme durability and strength.

15 One subset of polyamides, the nylons, is one of the most commonly created subsets of synthetic polymers. Nylons are typically condensation copolymers formed by reaction of dicarboxylic acids with diamines or by ring opening of lactams. Various nylon polymers can be created by adjusting the number of carbons. Conventional nomenclature designates in these various nylons and polyamides specify the diamine first and the diacid
20 second. Therefore, the most commercially common variant of nylon, nylon 6-6, has six carbons donated by the diamine, and six carbons from the diacid, and nylon 6-12 would have six carbons donated by the diamine and twelve carbons donated from the diacid. Distinct from nylon 6-6, nylon-6 is a homopolymer formed by a ring-opening polymerization. An example of this is nylon-6 produced by polymerizing caprolactam. . Because each variant
25 has a differing chemical structure, the physical properties of the nylons differ with regard to their impact resistance, tensile strength, elasticity, tear strength, melt temperature, color fastness, and other properties.

 Olefin-maleic anhydride polymers (OMAP) are formed by copolymerizing maleic anhydride with olefin monomers. Examples of such olefins include ethylene,
30 propylene, isobutylene, butene-1, octene, butadiene, styrene, isoprene, hexene, long chain alkenes (e.g. dodecene, dodecene-1, tetradecene), and the like. Some of these olefins are derived from natural gas and/or crude oil, whereas others are derived from natural substances or by biosynthesis. Examples of such copolymers include but are not limited to ethylene-

maleic anhydride, propylene-maleic anhydride, isobutylene-maleic anhydride copolymers and terpolymers such as ethylene-propylene-maleic anhydride terpolymer.

It will be appreciated that products which are made from polyamides are exposed to considerable stresses during manufacture and processing, and that a method for producing nylons or other polyamides with increased durability would be appreciated in the art, and that specific nylon formulations having increased durability will be greatly appreciated in the art.

SUMMARY

In one aspect, there is provided a thermoplastic pelletizable polymer composition comprising: (a) a polyamide; and (b) a polymer polymerized from maleic anhydride and an olefin selected from the group consisting of ethylene, propylene, isobutylene, butene-1, octene, butadiene, isoprene, hexane, dodecene, dodecene-1, and tetradecene; wherein the polyamide and the polymer are compounded.

In another aspect, there is provided a cross-linked polymer composition comprising: (a) a polyamide, and (b) a polyamide; and (b) a polymer polymerized from maleic anhydride and an olefin selected from the group consisting of ethylene, propylene, isobutylene, butene-1, octene, butadiene, isoprene, hexane, dodecene, dodecene-1, and tetradecene; wherein the polyamide and the polymer are compounded at a processing temperature wherein the processing temperature is sufficient to promote cross-linking.

In another aspect, there is provided a method of preparing a compounded polyamide comprising: compounding a polyamide mixture comprising a polyamide and an olefin-maleic anhydride copolymer, wherein the olefin is selected from the group consisting of ethylene, propylene, isobutylene, butene-1, octene, butadiene, isoprene, hexane, dodecene, dodecene-1, and tetradecene, at a processing temperature.

In another aspect, there is provided a method of producing a compounded polyamide, comprising compounding a polyamide mixture, where the polyamide mixture comprises an olefin-maleic anhydride copolymer with the olefin selected from the group consisting of ethylene, propylene, isobutylene, butene-1, octene, butadiene, isoprene, hexane, dodecene, dodecene-1, and tetradecene; a glass fiber and; one or more stabilizing agents at a temperature of between about 230°C and about 300°C.

In another aspect, there is provided a compounded polyamide produced by a process comprising compounding a polyamide mixture, comprising a polyamide and an olefin-maleic anhydride copolymer, wherein the olefin is selected from the group consisting of ethylene, propylene, and isobutylene at a processing temperature.

In another aspect, there is provided an article comprising the compounded polyamide or the polymer composite as defined above, wherein the article is selected from the group consisting of carpet fiber, apparel, an airbag, a tire, a rope, a conveyor belt, a hose, luggage, a molded auto part, a molded gun frame, a molded electrical part, a molded tool handle, toothbrush, a comb, a hairbrush, a food packaging film, an oil-resistant gasket, and bullet-resistant materials.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 Shows reduction of viscosity at high shear resulting from compounding a nylon (e.g. nylon-6) with EMA.

DESCRIPTION

The disclosure of the present application provides for compositions comprising polyamides with such olefin-maleic anhydride polymers (OMAP).

The disclosure of the present application also provides various methods for producing compounds of polyamides with ethylene maleic anhydride copolymers (EMA). Specifically, at least one embodiment of the present disclosure relates to methods for the reaction of nylon-like materials with ethylene maleic anhydride copolymers. At least one embodiment of the present disclosure involves processing methods such as extrusion compounding using equipment known to one skilled in the art. In the plastics industry, compounding is a process that mixes one or more polymers with one or more additives to produce plastic compounds in one or more steps. The feeds may be pellets, powder and/or liquids, but the product is usually in pellet form, to be used in other plastic-forming processes such as extrusion and injection molding. Machine size varies from tiny lab machines to the biggest extruders in the industry, running as much as 20 tons per hour. Usually twin-screw extruders are preferred because they give better mixing at lower melt temperatures. Most of

these have screws and barrels made up of smaller segments (mixing, conveying, venting and additive feeding) so that the design and sequence of addition of each of the ingredients in the formulation can be changed to meet the production and product needs. Other equipment such as single-screw extruders, oscillating screw extrusion, continuous mixers, Banbury mixers, and planetary extruders can be used for compounding as well. The additional components to be mixed and/or compounded (viscosity modifiers, additive carriers, and the like) and the processing parameters such as temperature of each of the zones, feed rates, residence time

and screw speed can be modified by the person skilled in the art for each application.. The method of producing compounds of polyamides according to at least one embodiment of the present application results in a compounded polymer with improvements in properties and performance such as increased stretch performance, impact strength, creep resistance, and resistance to anti-freeze degradation due to hydrolysis of the compound formed by reacting polyamide with olefin-maleic anhydride polymer.

According to at least one embodiment of the method of producing compounded polyamides of the present disclosure, the method comprises the step of compounding a polyamide with an ethylene maleic anhydride copolymer in a twin screw extruder or other processing method listed in the previous paragraph. Such pellets are subsequently processed by a plastic processing method such as injection molding, blown or cast film, sheet extrusion, thermoforming, or blow molding, into a finished article such as bottle, molded part, film, sheet, fabric, filament, fiber, etc.

Another embodiment includes directly extruding such a reaction mixture into a finished article such as a filament, fiber, film, sheet, and molded part.

In producing compounds of the present disclosure, a polyamide may be any appropriate polyamide as described herein. For instance, in an exemplary embodiment, the polyamide may be a nylon, such as nylon-6 or nylon 6-6. Additionally, polyamides used in at least one embodiment of the method of producing a compound polyamide may be aliphatic, alicyclic and aromatic polyamides such as one or more of nylon 6-12, nylon 4-6, nylon 9 nylon 10, nylon 6-9, nylon 11, nylon 12, nylon 5-10, nylon-meta-xylene diamine (nylon-MXD6), Kevlar® (DuPont), Nomex® (DuPont), Ixef® (Solvay Advanced Polymers), Trogamid® (Evonik Degussa), and Amodel® (Solvay Advanced Polymers). Further, according to at least one exemplary embodiment of the method of producing a compounded polyamide, the olefin-maleic anhydride like an ethylene maleic anhydride alternating copolymer (EMA) may be used in the treatment method in a molar ratio of ethylene to maleic anhydride of about 1:1. In alternative embodiments, the olefin-maleic anhydride like an ethylene maleic anhydride alternating copolymer (EMA) used in the treatment method in a molar ratio of ethylene to maleic anhydride of about 1:99 to about 99:1 may be utilized. Further alternative embodiments employ non-alternating copolymers or random copolymers with a molar ratio of ethylene to maleic anhydride range of about 1:50 to about 50:1; about 1:20 to about 20:1; about 1:10 to about 10:1; about 1:5 to about 5:1; and about 1:2 to about 2:1. In yet another embodiment, non-alternating copolymers or random copolymers may be utilized.

Additionally, according to at least one exemplary embodiment, the olefin-maleic anhydride selected for reaction with a polyamide has a weight average molecular weight of in the range of about 300 to about 10 million; about 10,000 to about 1 million; about 20,000 to about 800,000; about 40,000 to about 600,000; about 50,000 to about 500,000; or about 60,000 to about 400,000. For example, according to at least one exemplary embodiment, the EMA selected may have a molecular weight of about 60,000 such as that sold under the trademark ZeMac® E-60 (E60), or the EMA selected may have a molecular weight of about 400,000 such as that sold under the trademark ZeMac® E-400 (Vertellus Specialties Inc.) (E400). Moreover, the EMA may be used in an exemplary embodiment of the method of producing a compounded polyamide at a concentration of between about .01% to about 20.0% w/w; about 0.02% to about 0.5%; about 0.05% to about 7.0% w/w; about 0.1% to about 5.0% w/w; or about 0.5% to about 3.0% w/w.

According to at least one optional embodiment, a stabilizer package is added into the formulation, the stabilizer package comprising additives used individually or in combination with one another. According to one such embodiment, the additives may comprise phenolic antioxidants, phosphites, cuprous iodide (CuI), potassium iodide (KI), and/or other stabilizers. Optionally, the stabilizing package may comprise about 0.01% to about 5.0% w/w of the overall reaction mixture; about 0.1% to about 2.0% w/w; or about 0.5% to 1.0% w/w.

Several illustrative embodiments of the invention are described by the following enumerated clauses:

1. A thermoplastic pelletizable polymer composition comprising:
 - (a) a polyamide; and
 - (b) a polymer polymerized from maleic anhydride and an olefin; wherein the polyamide and the polymer are compounded.
2. The thermoplastic pelletizable polymer composition of clause 1 wherein the polyamide is selected from the group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, nylon-9, nylon-10, nylon-11, nylon-12, nylon 6-10, aromatic polyamides, elastomeric polyamides, and mixtures thereof.
3. The thermoplastic pelletizable polymer composition of clause 2 wherein the polyamide is selected from the group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, and mixtures thereof.
4. The thermoplastic pelletizable polymer composition of clause 1 wherein the olefin is selected from the group consisting of ethylene, propylene, isobutylene,

butene-1, octene, butadiene, styrene, isoprene, hexene, dodecene, dodecene-1, and tetradecene.

5. The thermoplastic pelletizable polymer composition of clause 1 wherein the olefin is ethylene.

5 6. A cross-linked polymer composition comprising:

(a) a polyamide, and

(b) a polymer polymerized from maleic anhydride and an olefin; wherein the polyamide and the polymer are compounded at a processing temperature wherein the processing temperature is sufficient to promote cross-linking.

10 7. The cross-linked polymer composition of clause 6 wherein the polyamide is selected from the group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, nylon-9, nylon-10, nylon-11, nylon-12, nylon 6-10, aromatic polyamides, elastomeric polyamides, and mixtures thereof.

8. The cross-linked polymer composition of clause 6 wherein the
15 polyamide is selected from the group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, nylon-11, and mixtures thereof.

9. The cross-linked polymer composition of clause 6 wherein the olefin is selected from the group consisting of ethylene, propylene, isobutylene, butene-1, octene, butadiene, styrene, isoprene, hexene, dodecene, dodecene-1, and tetradecene.

20 10. The cross-linked polymer composition of clause 6 wherein the olefin is ethylene.

11. A method of preparing a compounded polyamide comprising the steps of:

forming a polyamide reaction mixture by contacting the polyamide
25 with an olefin-maleic anhydride copolymer; and
compounding the polyamide reaction mixture at a processing temperature.

11a. A method of preparing a compounded polyamide comprising:
compounding a polyamide mixture comprising a polyamide and an
30 olefin-maleic anhydride copolymer at a processing temperature.

12. The method of clause 11 or 11a, wherein the olefin is selected from the group consisting of ethylene, propylene, isobutylene, butene-1, octene, butadiene, styrene, isoprene, hexene, dodecene, dodecene-1, and tetradecene.

13. The method of clause 11 wherein the olefin is ethylene.

14. The method of clause 11 or 11a, wherein the polyamide is a nylon.
15. The method of clause 11 or 11a, wherein the polyamide is selected from the group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, nylon-9, nylon-10, nylon-11, nylon-12, nylon 6-10, aromatic polyamides, elastomeric polyamides, and mixtures thereof.
16. The method of clause 11 or 11a wherein the polyamide is selected from the group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, and mixtures thereof.
17. The method of clause 13, wherein the olefin-maleic anhydride copolymer has a ratio of ethylene to maleic anhydride of 1:1.
18. The method of clause 17, wherein the olefin-maleic anhydride copolymer has a molecular weight of about 300 to 1,000,000.
19. The method of clause 17, wherein the olefin-maleic anhydride copolymer has a concentration of about 0.01% to about 0.5%, about 0.5% to about 1.0%, about 1.0% to about 1.5%, or 1.5% to about 3.0% w/w.
20. The method of clause 11 or 11a, wherein the processing temperature is about 230°C to about 300°C.
21. The method of clause 11 or 11a, wherein the step of forming the polyamide reaction mixture further comprises the step of compounding a polyamide with a glass fiber.
22. The method of clause 21, wherein the glass fiber has a concentration of about 0.1% to about 30%.
23. The method of clause 11 or 11a, where wherein the step of forming a polyamide reaction mixture further comprises the step of contacting a polyamide with one or more stabilizing agents.
24. The method of clause 23, wherein each of the one or more stabilizing agents is independently selected from a group consisting of cuprous iodide, potassium iodide, tris (2,4-di-tert-butylphenyl)phosphite, and N,N'-hexane-1,6-diylbis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionamide)).
25. The method of clause 23, wherein each of the one or more stabilizing agents independently has a concentration of about 0.01 to about 1.0% w/w.
26. A method of producing a compounded polyamide, comprising the steps of:

providing a polyamide mixture, where the polyamide mixture comprises an olefin-maleic anhydride copolymer; a glass fiber and; one or more stabilizing agents; and

compounding the polyamide reaction mixture at between about 230°C and about 300°C .

26a. A method of producing a compounded polyamide, comprising compounding a polyamide mixture, where the polyamide mixture comprises an olefin-maleic anhydride copolymer; a glass fiber and; one or more stabilizing agents at a temperature of between about 230°C and about 300°C.

27. A compounded polyamide produced by a process comprising the steps of:

forming a polyamide reaction mixture, comprising a polyamide and an olefin-maleic anhydride copolymer;

compounding the polyamide reaction mixture at a processing temperature.

27a. A compounded polyamide produced by a process comprising compounding a polyamide mixture, comprising a polyamide and an olefinic-maleic anhydride copolymer at a processing temperature.

28. The compounded polyamide of clause 27 or 27a wherein the olefin-maleic anhydride polymer is an ethylene-maleic anhydride polymer.

29. The compounded polyamide of clause 27 or 27a, wherein the polyamide is selected from the group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, nylon-9, nylon-10, nylon-11, nylon-12, nylon 6-10, aromatic polyamides, elastomeric polyamides, and mixtures thereof.

30. The compounded polyamide of clause 27 or 27a wherein the polyamide is selected from the group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, and mixtures thereof.

31. The compounded polyamide of clause 27 or 27a, wherein the polyamide is selected from a group consisting of nylon-6 and nylon 6-6.

32. The compounded polyamide of clause 28, wherein the ethylene maleic anhydride copolymer has a ratio of ethylene to maleic anhydride of 1:1.

33. The compounded polyamide of clause 28, wherein the ethylene-maleic anhydride copolymer has a molecular weight of about 300 to 1,000,000.

34. The compounded polyamide of clause 27 or 27a, wherein the ethylene-maleic anhydride has a concentration of about 0.01% to about 0.5%, about 0.5% to about 1.0%, about 1.0% to about 1.5%, or 1.5% to about 3.0% w/w.

35. The compounded polyamide of clause 27 or 27a, wherein the processing temperature is from about 230°C to about 300°C.

36. The compounded polyamide of clause 27 or 27a, wherein the polyamide reaction mixture further comprises a glass fiber.

37. The compounded polyamide of clause 36, wherein the glass fiber has a concentration of about 0.1% to about 30%

38. The compounded polyamide of clause 27 or 27a, wherein the polyamide reaction mixture further comprises one or more stabilizing agents.

39. The compounded polyamide of clause 38, wherein the one or more stabilizing agents are each independently selected from the group consisting of cuprous iodide, potassium iodide, tris(2,4-di-tertbutylphenyl)phosphite, and N,N'-hexane-1,6-diylbis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionamide)).

40. The compounded polyamide of clause 39, wherein the one or more stabilizing agents each independently has a concentration of about 0.01 % w/w to about 1.0% w/w.

41. The compounded polyamide of clause 33, wherein the ethylene maleic anhydride copolymer has a molecular weight of about 60,000 to about 400,000.

42. The compounded polyamide of clause 13, wherein the ethylene maleic anhydride copolymer has a molecular weight of about 60,000 to about 400,000.

43. The compounded polyamide or polymer composite of any one of the preceding clauses wherein the polyamide is a recycled nylon.

44. An article comprising the compounded polyamide or the polymer composite of any one of clauses 1 to 42, wherein the article is selected from the group consisting of carpet fiber, apparel, an airbag, a tire, a rope, a conveyer belt, a hose, luggage, a molded auto part, a molded gun frame, a molded electrical part, a molded tool handle, toothbrush, a comb, a hairbrush, a food packaging film, an oil-resistant gasket, and bullet-resistant materials.

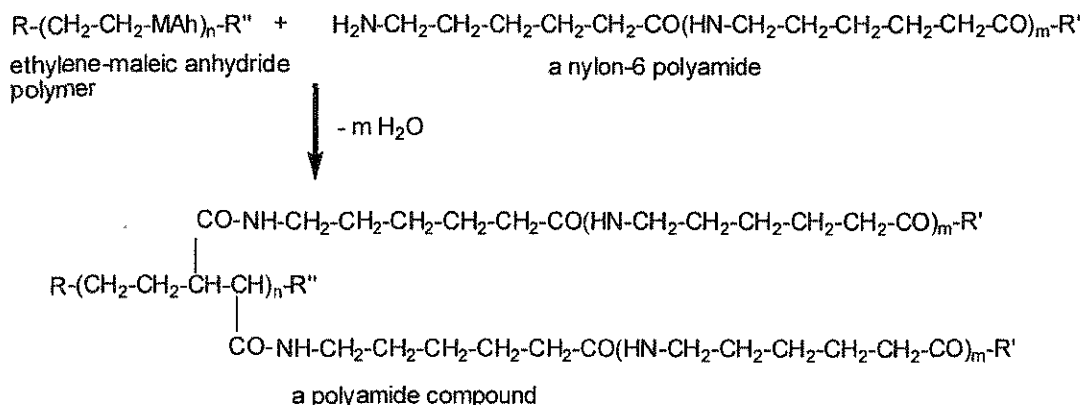
Further, according to additional exemplary embodiments, UV stabilizers and absorbents, halogenated or non-halogenated flame retardant additives; reinforcements such a mineral or fibers, fabrics, roving filaments, tubes and yarns, made from glass, carbon, graphite, cellulose and other natural materials; and/or aromatic high melting polymers

(sometimes referred to as aramids) are included within the reaction mixture. Plasticizers, lubricants, rheology modifiers, friction modifiers, and other additives known to one skilled in the art may also be optionally added to the mixture depending on the application requirements.

5 According to at least one step of forming a polyamide reaction mixture, the combination of the component parts may be accomplished by any type of applicable extruder, such as a single or double screw extruder, or an applicable extruder used in conjunction with a mixer.

10 While conducting the compounding step in an embodiment of the method of producing a compounded polyamide of the present disclosure, the first temperature may be any temperature sufficient to melt the polyamide and promote the compounding of a polyamide with EMA. In an exemplary embodiment, with nylon-6, the temperature settings on the extruder and the processing temperature may be about 230°C to about 300°C. In other embodiments, the temperature settings and compounding temperature may be from about
15 230°C to about 260°C or from about 220°C to 260°C. For nylon 6-6, such a temperature may range from 250°C to 310°C or from 240°C to 280°C. However, for higher melting polyamides such as Nomex® polymer, such processing temperatures are likely in the range of 280°C to 380°C. For elastomeric polyamides such as nylon-9, nylon-10, nylon-6,10, nylon-11 and nylon-12, the range may be considerably less, in the range of 150°C to 250°C. It is
20 recognized that the upper value of the compounding temperature, may be bound by the temperature at which degradation of the nylon being compounded becomes significant the lower value may be bound by the melting or softening point of the nylon.

 Without being bound by theory, it is believed that nylons (also called polyamides) require the presence of a free amine group in order for it to react with the
25 anhydride groups of the olefin-maleic anhydride copolymer (see the formula below). Illustratively, grade Ultramid B3S, which has free amine groups and is not end capped, reacts whereas Ultramid B27 which is end capped has no free amine groups available for reaction.



In at least one embodiment of the method of compounding a polyamide, the step of forming a polyamide reaction mixture may further comprise the step of contacting a polyamide with a glass fiber. The introduction of glass fiber may occur before or after the compounding of the polyamide with EMA. The glass fiber may have a concentration of about 0.1% to about 60%; about 10% to about 50%. Further, in an exemplary embodiment of the present disclosure, a glass fiber may have a grade and size applicable with nylon compounding.

According to other exemplary embodiments, other reinforcements may be compounded with the polyamide, including carbon nano tubes, mica, talc, calcium carbonate, wollastonite, carbon fibers, Kevlar[®] fibers, nano-particles made from clay and other materials. Other embodiments include fabrics, roving filaments, tubes and yams, made from glass, cellulose and other natural materials, carbon, graphite, aromatic high melting polymers (sometimes referred to as aramids) and ceramics. A specific example is Kevlar[®] fibers, with a 12 micron diameter and 0.5 inch fiber length. Another example is a biaxially oriented glass fiber fabric such as VECTORPLY[™] E-LTM 3610.

An exemplary embodiment of the method of producing a compounded polyamide may also comprise the step of injection molding of the polyamide. Optionally, the polyamide may be combined with the EMA directly during injection molding.

As a result of producing a compounded polyamide by an embodiment of the method of the present disclosure, the treated polyamide (i.e. compounded polyamide) was found to exhibit increased impact strength and/or increased tensile strength as compared to uncompounded polyamide. The increased impact strength may be at least about 5%, at least about 10%, at least about 15%, at least about 20%, at least about 25%, at least about 28%, at least about 30%, at least about 33%, at least about 35%, at least about 40%, or at least about 50%, greater than the uncompounded polyamide.

According to at least one embodiment of a compounded polyamide of the present disclosure, a compounded polyamide formed by the process of compounding the polyamide with an EMA is disclosed. Further optionally, the polyamide may be a nylon-6 or a nylon-66 and the EMA has a weight molecular weight of about 60,000 to about 400,000.

- 5 The polyamide may also be nylon-9, nylon-12, nylon-11, nylon 4-6, or any of the polyamides listed herein. In another illustrative embodiment, the polyamide compounded with the EMA in any of the embodiments described herein may be a recycled nylon.

Recycled nylon/polyamide can include many different types of materials of varying quality from various industries. The recycled polyamide may be from post-industrial
10 sources or post-consumer sources or from a combination of both. An example of a high quality recycled nylon is non-colored nylon that has sufficient molecular weight for injection molding. Another illustrative recycled nylon is "Off-spec" or "non-prime" polyamide/nylon that does not meet specifications for its intended use or is transition material that is produced during the change over between production of one grade of nylon and another grade on
15 nylon. This type of recycled nylon material product is priced from about 2-5% below the price of prime nylon to about 25% below the price of prime nylon depending on market conditions. Much of the recycled nylon of lower quality that is available currently goes into landfills. Illustrative sources of lower quality recycled nylon are the textile or the hosiery industry. Another source is recycled fish nets. Much of this lower quality material is a low
20 viscosity nylon, which usually cannot be used for injection molding applications without modification as describe herein. Recycled nylon from the automotive industry is typically black and cannot be used for non-black applications. The recycled nylon may also contain one or more non-polyamide polymers. In one illustrative example carpet waste usually contains 80-85% polyamide, remaining material being polyester, polypropylene and some
25 polyurethane. Due to poor mechanical performance such carpet waste is not typically reused and ends up in landfills. Depending upon the performance and quality of the material, polyamides prices vary. By compounding these types of recycled polyamides with EMA copolymers as described herein, these materials can be used for more value-added applications.

- 30 According to at least one additional embodiment of the compounded polyamide of the present disclosure, a reacted or compounded polyamide may be incorporated into any product where increased performance over uncompounded polyamide is desired. In an exemplary embodiment, compounded polyamide may be incorporated into any one of carpet fiber, apparel, airbags, tires, ropes, conveyer belts, hoses, luggage, molded

products (such as auto parts, gun frames, electrical parts, and tool handles), personal hygiene products (such as toothbrushes), medical devices and surgical products, food packaging films, oil-resistant gaskets, defense & aerospace products, and bullet-proof materials.

According to at least one embodiment, cross-linked compositions of this disclosure prepared by using relatively higher levels of an olefin-maleic anhydride polymer (OMAP) in a polyamide matrix are used for cast or thermally laminated nylon applications. For achieving such objectives, the ratio of the OMAP is in the range of about 10% to about 50% w/w, or about 10% to about 20%. Applications for a cross-linked composition of this variety are optionally processed by methods typically used for thermoset polymers, some of which use reinforcement with fabrics made from glass fibers. Such polymers can be useful for applications ranging from metal replacement (e.g. mechanical parts, medical devices, and the like) to use in transportation. Other uses include applications in defense and aerospace. In other embodiments of these cross-linked compositions, the olefin-maleic anhydride polymer is an alternating 1:1 ethylene-maleic anhydride polymer.

As used herein, the term "compounding" generally refers to a process that mixes one or more polymers with one or more additives to produce plastic compounds in one or more steps. The materials to be mixed may be in the form of pellets, powders and/or liquids. Typically the product is in pellet form for use in other plastic-forming processes such as extrusion and injection molding

METHODS AND EXAMPLES

MATERIALS

Polyamide 6 (grade Ultramid™ B3S) and polyamide 6,6 (grade Ultramid™ A34) both prime quality from BASF were used as received, as was recycled polyamide 6. Care was taken to ensure that all grades stayed dry. A 1:1 ethylene-maleic anhydride alternating copolymer grade ZeMac™ E60 (E60) from Vertellus Specialties Inc. with a weight average molecular weight (Mw) of 60,000 was used in these illustrative examples. A 1:1 ethylene-maleic anhydride alternating copolymer grade ZeMac™ E400 (E400) from Vertellus Specialties Inc. with a weight average molecular weight (Mw) of 400,000 was also used in illustrative examples. A stabilizer package, consisting of 0.09% potassium iodide (KI), 0.01% cuprous iodide (CuI), 0.4% Irgafos™ 168 (phosphite stabilizer), and 0.5% Irganox™ 1098 (hindered phenol antioxidant), was used with all compounded samples.

GENERAL COMPOUNDED POLYAMIDE PREPARATION

Composite pellets of compounded polyamide with E60 or E400 were prepared in a counter-rotating inter-meshing twin screw extruder (Bertstroff 25 mm. 32D). Polyamide-6 and recycled polyamide-6 samples were run using the temperature settings of 235, 245, 255, 245, 240, 240, 240, 240°C, while polyamide-6,6 samples were compounded using temperature settings of 250, 265, 275, 270, 270, 270, 270, 280°C. For GF-reinforced runs the glass fiber, at a loading level of 30%, was fed downstream with a side feeder.

GENERAL TESTING METHODS

Tensile, flexural, notched Izod impact strength and melt flow index measurements were carried out using standard ASTM methods D-638, D-790, D-256 and D-1238 respectively at 23 °C. Charpy impact strength was measured using the ISO-179-2/2 method at room temperature (23 °C) and at -30 °C. Heat deflection/distortion temperature was measured using ASTM method D-648. These mechanical and thermal tests were carried out without additional drying, the samples were used as molded after conditioning the test specimen as per ASTM protocol. Water absorption tests were carried after drying to equilibration to ensure that all the absorbed water has been removed and all the samples are dry. The percent increases in the amount of water absorbed were determined after 24, 48 and 72 hours.

PRIME POLYAMIDE-6

Polyamide-6 was compounded with 1% ethylene-maleic anhydride copolymer, with and without 30% glass fiber. The tensile strength, elongation and notched Izod impact strength of the resulting compounded materials are shown in TABLE 1 below.

TABLE 1

Formulation	Nylon-6 + no additive	Nylon-6 + 1% E60	Nylon-6 + 30% Glass Fiber + no additive	Nylon-6 + 30% Glass Fiber + 1% E60
Tensile Strength at Strain (MPa)	50	70.5	69	79
Tensile Elongation at Break (%)	5.9	8.0	4.9	9.2
Tensile Elongation at Yield (%)	5.2	7.9	4.9	8.8
Tensile Modulus (MPa)	1150	1200	2250	2400
Notched Izod (ft-lb./in.)	1.30	1.55	1.50	2.00

Notched Izod (J/m.)	69	83	80	107
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The results of tensile strength, elongation and notched Izod impact strength shown in TABLE 1 demonstrate that the alternating copolymer enhances all three properties with and without 30% fiber glass. Typically when tensile strength is increased in most plastics with some sort of modification, elongation decreases and vice versa. It has been discovered that compounding the polyamide with EMA results in both tensile strength and elongation increases simultaneously. It is believed that these observations show that the basic structure of at least some of the polyamide is being modified into a highly branched structure with very high molecular weight which results in a stronger and tougher compounded polyamide.

During compounding an increase in both viscosity and torque is observed. When a polyamide grade with no end groups was used, no increase of viscosity or mechanical properties was observed. It is believed that this indicates that no amidation reaction can occur in the absence of amine end groups on the polyamide. It was also observed that cross-linking can occur at high loadings of the EMA (>10%) and the resulting compounded material does not flow. Use of other materials which have one reactive group i.e., one anhydride, (for example polyethylene grafted with maleic anhydride) or modifier with one reactive group at each end show only a slight increase in viscosity and little increase in mechanical properties compared to the use of EMA copolymers (unique structures with thousands of reactive groups on each molecular chain) disclosed herein. This increase in viscosity also results in a reduction of melt flow rate of polyamide-6 as shown in TABLE 2.

TABLE 2

Additive	Melt Flow Rate @ 235°C & 1kg (g/10min)
not compounded	9.7
0.1% E60	4.3
0.3% E60	1.7
0.5% E60	1.0

PRIME POLYAMIDE-6,6

It was observed during compounding that polyamide 6,6 generated higher viscosity increase and torque at the same loading levels of EMA. This may be attributed

partly to the higher temperature at which polyamide-6,6 is processed compared to polyamide-6 but also because it is understood that polyamide-6,6 typically has amine end groups at both ends. Similar to the results for polyamide-6, mechanical properties of polyamide-6,6 are also improved while the melt flow rate decreases. In addition we observed an increase in heat deflection temperature as shown in TABLE 3 below.

TABLE 3

Additive	Melt Flow Rate @ 275°C & 5kg (g/10min)	Heat Deflection Temp. °C at 1.82 Mpa (264 psi)
not compounded	142.05	59.6
no additive	29.06	70.5
0.1% E60	21.12	74.1
0.3% E60	8.98	71.0
0.5% E60	2.27	71.3

RECYCLED NYLON-6

The recycled polyamide used for this study was primarily nylon-6 from an industrial source. Due to the presence of some nylon-6,6 in this recycled polyamide, the melt flow rate is lower than what would typically be expected from a recycled stream with just polyamide-6. During compounding it generated less torque than the corresponding prime nylon-6. Without being bound by theory, it is believed that the lower torque is due to the expected degradation caused by additional heat history of the recycled nylon-6 compared to prime nylon-6. TABLE 4 shows the decrease of melt flow rate in recycled polyamide compounded with E60. It is believed that this decrease in melt flow rate is due to chain extension and the resultant branching. The resulting shear thinning enabled excellent injection molding contrary to what one might expect from the fractional melt flow rates obtained when ASTM test specimens were molded.

TABLE 4

Additive	Melt Flow Rate (ASTM D-1238) 235°C w/1kg (g/10min)
no E60	13
no additive	6.2
0.1% E60	1.17

0.3% E60	0.80
0.5% E60	0.44
1% E60	0.5
3% E60	1.6
Prime Nylon-6	9.65

The tensile strength of injection molded specimens was measured as described in protocol ASTM D638. The results are shown in TABLE 5. Various commercial grades of prime polyamide-6 grades differ slightly in terms of tensile strength values as indicated on the specification data sheets provided by the supplier.

As the data in TABLE 5 shows, after reactive compounding of the recycled polyamide with the ethylene-maleic anhydride alternating copolymer to yield compounded recycled polyamide, the tensile strength values match or approach the range of values of prime polyamide grades (75 to 85 MPa). Other properties of the compounded recycled polyamide are also improved. TABLE 6 shows the flexural modulus properties of recycled polyamide as a function of the addition of low loadings of the same alternating copolymer of ethylene and maleic anhydride.

This increase in flexural modulus of the compounded recycled polyamide matches or exceeds the similar range of flexural modulus of the various grades of prime polyamide-6 available from different suppliers. An increase in flexural strength at break is also observed for the compounded recycled polyamide as shown in TABLE 6. It is seen from the values for both flexural modulus and flexural strength at break shows that the values increase as a function of the amount of added alternating copolymer from 0.1 to 0.5%. The values do not appear to increase further when the percentage of added E60 is increased further.

TABLE 5 Increase of tensile strength of recycled polyamide due to E60 reaction.

Compounded Recycled Polyamide Additive	TENSILE PROPERTIES (ASTM D638)	
	Tensile Strength @ Yield (MPa)	Elongation @ Break (%)
no E60	61.1	19.47
no additive	78.2	18.24
0.1% E60	78.5	12.66
0.3% E60	80.2	17.58
0.5% E60	79.5	12.79

1% E60	82.0	29.17
3% E60	80.4	15.91
Prime Nylon-6	83.6	12.41

TABLE 6 Increase of flexural modulus and strength of recycled polyamide due to E60 reaction.

Additive	FLEX ASTM D790	
	Flex. Modulus (Mpa)	Flex Strength @ Break (Mpa)
no E60	2385	77.2
no additive	2632	102.5
0.1% E60	2689	105.7
0.3% E60	2749	114.0
0.5% E60	3016	121.1
1% E60	2867	110.8
3% E60	2866	113.3
Prime Nylon-6	2796	113.8

The Izod impact strength for compounded recycled polyamide was measured according to protocol ASTM D256. The results measured at room temperature (23°C) and at -30°C are shown in TABLE 7. The results show an increase in as a function of the addition level of the alternating copolymer at both room temperature and at -30°C. What is surprising, however, is that the values measured at low temperature unexpectedly are higher than the values measured at room temperature and are higher than the values measured for prime nylon-6.

The Charpy impact strength measured at 23°C and -30°C are shown in TABLE 8. Increases in the Charpy impact strength are observed compared to without adding the alternating copolymer. However the increase is not progressive at 0.5% loading level at 23°C. When compared to the values for prime polyamide, they are exceeded at 23°C for all three loadings but only at 0.5% at -30°C.

TABLE 7 Increase of Izod impact strength of recycled polyamide compounded with E60 measured at 23°C and -30°C.

Additive	IZOD IMPACT (ft-lb/in) ASTM D256	
	@ 23°C	@ -30°C
no E60	0.52	0.42 (CB)
no additive	0.87	0.45 (CB)
0.1% E60	0.96	1.01 (CB)
0.3% E60	1.05	1.30 (CB)
0.5% E60	1.32	1.39 (CB)
Prime Nylon-6	1.33 (CB)	0.46 (CB)

TABLE 8 Increase of Charpy impact strength of recycled polyamide compounded with E60 measured at room temperature (23°C) and -30°C.

Additive	CHARPY IMPACT ISO-179-2/2 (KJ/m ²)	
	@ 23°C	@ -30°C
no E60	33.8	24.7
no additive	46.9	19.9
0.1% E60	40.3	23.7
0.3% E60	48.4	29.2
0.5% E60	40.1	39.4
Prime Nylon-6	32.2	22.3

5

It is appreciated that the addition of the polar E60 as an additive can result in an increase of the water absorption of the compounded polyamide samples. Water absorption measurements were carried out after drying the sample to equilibration to ensure that they were dry. The amount of water absorbed was determined after 24, 48 and 72 hours. As shown in TABLE 9 there is only a small increase in water absorption observed in the samples of polyamide compounded with the E60 copolymer.

10

TABLE 9

Additive	WATER ABSORPTION (%)		
	24 Hrs.	48 Hrs.	72 Hrs.
no E60	1.03	1.48	1.79
no additive	1.02	1.42	1.77
0.1% E60	1.28	1.69	2.24
0.3% E60	0.88	1.32	1.56
0.5% E60	0.69	1.10	1.97
1% E60	1.09	1.50	1.8
3% E60	0.87	1.38	1.82

EXAMPLE

In determining the effect of ethylene maleic anhydride copolymers (EMA) on nylon-6 and nylon 6-6, both types of nylon were compounded with 30% glass fiber, 1.4% EMA, and a stabilizer package comprising the combination of compounds disclosed in

- 5 TABLE 2. Pellets of the compounded nylon were then molded into ASTM test specimens and the following properties were tested: Notched Izod Impact Strength, Unnotched Izod Impact Strength, as well as for tensile properties, strain at break and strain at yield. Compounding of the nylon, glass fiber, EMA and the stabilizer package was performed on a twin screw extruder with all components added to a hopper. According to the exemplary
- 10 embodiment, processing melt temperature of the nylon mixture was 260°C for nylon-6,6 compounds and 240°C for nylon-6 compounds. Illustrative results of the analysis of the properties of compounded nylon as compared to the uncompounded nylon are shown in TABLE 10. The fiberglass grade used in the mixture was a high performance E-glass chopped strand with a 10 μ diameter and a 4.5 mm length, typically used in extrusion
- 15 compounding with polyamide resin systems.

TABLE 10

Comparison of Physical Properties of Nylon Compounds

Formulation (all with 30% E-Glass Fiber*)	Nylon-6 no EMA	Nylon-6 w/ E400	Nylon-6 w/ E60
Tensile Strength (MPa)	176.3	162.1	160.9
Tensile Elongation (%)	3.70	4.86	5.50
Notched Izod (ft-lb./in.)	1.80	1.62	2.30
UnNotched Izod (ft-lb./in.)	20.5	17.5	23.1

TABLE 11

Stabilizer Composition as a Function of Total Compound Weight

Compound	% w/w to total 100%
Cuprous Iodide	0.01%
Potassium Iodide	0.09%
Irgafos 168 (phosphite)	0.40%
Irganox 1098 (hindered phenol)	0.50%

In each of the following TABLES 12-15, except for the first entry, each polymer was compounded with the stabilizer composition shown in TABLE 11

TABLE 12 - Melt Flow Rate of Recycled Nylon-6 @ 235°C & 1kg (g/10min)

Not compounded	No additive	0.1% E60	0.3% E60	0.5% E60	1% E60	3% E60
13.0	6.2	1.2	0.8	0.4	0.5	1.6

TABLE 13 - Tensile Strength of Recycled Nylon-6 (MPa)*

Not compounded	No additive	0.1% E60	0.3% E60	0.5% E60	1% E60	3% E60
61.1	78.2	78.5	80.2	79.5	82.0	80.4

* Values for Prime Nylon are in the range of about 65-71 MPa

TABLE 14 - Flex Modulus of Recycled Nylon-6 (MPa)*

Not compounded	No additive	0.1% E60	0.3% E60	0.5% E60	1% E60	3% E60	1% E400
2385	2632	2689	2749	3016	2867	2866	3000

* Values for Prime Nylon are in the range of about 2600-2800 MPa

TABLE 15 - Flex Strength @ Break of Recycled Nylon-6 (MPa)*

Not compounded	No additive	0.1% E60	0.3% E60	0.5% E60	1% E60	3% E60	1% E400
77.24	102.52	105.70	113.95	121.09	110.78	113.3	119.15

* Values for Prime Nylon are in the range of about 100-108 MPa

TABLE 16

At 0.1% ZeMac E-60 in Prime Nylon 6-6 (BASF's Ultramid A34), the compounded polyamide shows improvement of several properties:

	Tensile Properties				Flexural		Izod Impact		Charpy Impact		HDT	MFI	Specific Gravity
	ASTM D638				ASTM D790		ASTM D256		ISO-179-2/2		ASTM D648	ASTM D1238	ASTM D792
Additive	Modulus (MPa)	Stress @ Yield (MPa)	Stress @ Break (MPa)	Strain @ Break (%)	Modulus (MPa)	Stress @ Break (MPa)	Room Temp (ft-lb/in)	-30°C (ft-lb/in)	Room Temp (KJ/m^2)	-30°C (KJ/m^2)	264 psi (°C)	275°C & 5Kg (g/10min)	(g/ml)
not compounded	2653	75.4	56.9	33.6	2787	100.8	0.54 (CB)	0.48 (CB)	36.00 (NB)	33.6 (NB)	59.6	142.1	1.14
0.1% E60	2719	84.8	66.1	13.1	2781	112.3	1.07 (CB)	0.42 (CB)	35.0 (NB)	35.8 (NB)	74.1	21.1	1.14

MFI – melt flow index, HDT – Heat Deflection Temperature, NB – no break, CB – complete break HB – half break

TABLE 17

Prime nylon-6 (BASF's Ultramid B3S) compounded with E60 shows improvement in the following properties:

	Tensile Properties		Flexural		Izod Impact	Charpy Impact		HDT	MFI
	ASTM D638		ASTM D790		ASTM D256	ISO-179-2/2		ASTM D648	ASTM D1238
Additive	Stress @ Yield (MPa)	Strain @ Break (%)	Modulus (MPa)	Stress @ Break (MPa)	-30°C (ft-lb/in)	23°C (KJ/m^2)	-30°C (KJ/m^2)	264 psi (°C)	235°C w/ 1kg (g/10min)
not compounded	83.6	12.4	2796.1	113.8	0.46 (CB)	32.2 (NB)	22.3 (CB)	62.1	9.65
0.1% E60	78.4	11.4	2680.2	105.4	0.38 (CB)	42.9 (NB)	24.4 (CB)	59.1	4.34
0.3% E60	78.8	14.5	2747.6	106.9	0.46 (CB)	44.6 (NB)	23.9 (CB)	55.3	1.73
0.5% E60	85.4	15.0	2992.0	121.3	0.61 (CB)	49.7 (NB)	27.0 (CB)	56.5	0.97

TABLE 18

Properties of prime nylon-6 (BASF's Ultramid B3S) compounded with 30% glass fiber and E60.

	Tensile Properties				Flexural			Izod Impact		Charpy Impact		HDT
	ASTM D638				ASTM D790			ASTM D256		ISO-179-2/2		ASTM D648
Additive	Modulus (MPa)	Stress @ Yield (MPa)	Stress @ Break (MPa)	Strain @ Break (%)	Modulus (MPa)	Stress @ Break (MPa)	Stress @ Yield (MPa)	Room Temp (ft-lb/in)	-30°C (ft-lb/in)	Room Temp (KJ/m ²)	-30°C (KJ/m ²)	264 psi (°C)
0.3% E60	5586	78.8	78.6	3.17	7263	112.6	24.6	1.13 (CB)	0.77 (CB)	6.24 (CB)	5.80 (CB)	198.8
0.5% E60	5547	82.9	82.5	3.34	6744	122.9	130.9	1.13 (CB)	0.73 (CB)	7.09 (CB)	7.62 (CB)	192.3

TABLE 19

Properties of prime nylon-6,6 (BASF's Ultramid A-34) with 30% glass fiber.

30% GF in Nylon 6-6 (Ultramid A34)	Tensile Properties				Izod Impact		Charpy Impact		Charpy	
	ASTM D638				ASTM D790		ASTM D256		ISO-179-2/2	
Additive	Tensile Modulus	Tensile Strength @ Yield	Tensile Stress @ Break	Tensile Strain (Elongation) @ Break	Modulus	Flex Strength @ Break	23°C	-30°C	23°C	-30°C
	(MPa)	(MPa)	(MPa)	(%)	(MPa)	(MPa)	(ft-lb/in)	(ft-lb/in)	(KJ/m^2)	(KJ/m^2)
0.3% E60	6548	97.1	97.7	2.86	7471	140.6	0.94 (CB)	0.71 (CB)	5.50 (CB)	5.68 (CB)
0.5% E60	5723	102.8	102.5	3.36	6873.	144.6	0.93 (CB)	0.67 (CB)	6.79 (CB)	6.82 (CB)

EXAMPLE

According to this example, the effect of reacting recycled nylon with varying ethylene maleic anhydride copolymers (EMA) was evaluated. According to at least one exemplary embodiment, recycled nylon was processed with EMA as discussed in further detail below, and the reaction product was evaluated for resistance to anti-freeze degradation due to hydrolysis and impact strength as compared with untreated recycled nylon. The results indicate that processing nylon and other polyamides with EMA can improve both the resistance to anti-freeze degradation due to hydrolysis properties and the impact strength of the composition over uncompounded polyamides.

Compounded nylon-6 exhibited an increase in notched Izod impact strength from 3 ft-lb/in for uncompounded nylon-6 to between 3.78 ft-lb/in and 4.72 ft-lb/in. In addition to the increase in resistance to anti-freeze degradation due to hydrolysis and impact strength, compounded nylon is expected to display an increase in tear strength, a reduction in creep, and a decrease of the coefficient of linear thermal expansion.

EXAMPLE

The properties of various nylon-6 (PA6) blends (as shown in TABLE 20) were tested with and without ethylene-maleic anhydride copolymer (EMA) to determine the effect that treatment of nylon-6 with EMA has on the physical characteristics of nylon-6. In performing the treatment of nylon-6, the nylon-6/EMA mixture was blended in a co-rotating twin screw extruder (Leistritz, ZSE, 27HP, D=40mm), and then injection molded with an injection molding machine (Cincinnati Milacron-Fanuc, Roboshot, 55USTON, 1.95oz) into standard tensile and impact bars. The compounding conditions in which nylon-6 was mixed are shown in TABLE 21. Additionally, the injection molding conditions are shown in TABLE 22. Further, prior to mixing, all nylon-6 were pre-dried at 85°C overnight. Properties of several nylon-6 blends with EMA are shown in TABLES 12-15

TABLE 20
Nylon Blend Components

Blend	Polymer Content [phr]	Filler Content [phr]	EMA Content [phr]
Nylon-6	100	0	0
Nylon-6 + EMA**	100	0	10
Nylon-6 + EMA	100	0	1
Nylon-6 + GF	67	33	0
Nylon-6 + GF + EMA**	70	30	10
Nylon-6 + GF + EMA*	70	30	1

TABLE 21 — PA6 Compounding Conditions

	Temp. [°C]	RPM	Torque [%]	Pressure [psi]	Feed [%]
Nylon-6 + GF	200-230-240	50	60	80	20
Nylon-6 + GF + EMA	200-230-240	65	30	310	20
Nylon-6 + EMA	200-230-240	65	30	350	25
Nylon-6	200-220-230	50	40	30	25

5

TABLE 22
Injection Molding Conditions

	Barrel Temp. [°F]	Mold Temp. [°F]	Cooling Time [sec]
Nylon-6 + GF	440-465	150	30
Nylon-6 + GF + EMA	440-465	150	30
Nylon-6 + EMA	440-465	150	30
Nylon-6	440-465	150	30

GF – glass fiber

All samples were tested for impact properties according to ASTM D256 with a
 10 2 lb-ft pendulum, and tensile properties according to ASTM D638 at a 50 mm/min cross-head
 speed. In determining these properties, Tensile Modulus (as shown in TABLE 1) indicates the
 force to bend. It will be appreciated that as the results increase, stiffness of the sample
 increases, while as the results lower, flexibility increases. As shown in TABLE 1, the strain at
 break was calculated as a percentage, where high numbers indicate stretchability before the
 15 sample breaks. Strain at yield, shown in TABLE 1, was calculated for each sample, indicating
 the force at apex prior to reduction. In other words, as the material stretches, it requires more
 force to stretch, until it reaches a "neck" point, where the sample thins out enough to require

less force to stretch. In general, it will be appreciated that brittle materials do not neck.

Further, as shown in TABLE 1, indicates the strain at yield, denoting the percentage change in length, where a higher value indicates the longer the sample must stretch before it finally breaks. Lastly, samples were tested for impact strength, which is the force required to break
5 the sample. This is a high speed impact test, in which the higher the number the higher the impact strength. Each of these tests were run 4-5 times and the average reported.

EXAMPLE

40 g. of nylon-6 pellets and 4 g. of ZeMac® E-60 (E60) were melt mixed in a Brabender
10 laboratory size mixing bowl, preheated to 245°C and mixed until all pellets were molten and the mixture well fluxed. At ratios of at and above 10% the ethylene-maleic anhydride copolymer did not flow, and appeared to crosslink the polyamide.

EXAMPLE

15 Molded tensile bars are immersed in radiator fluid (commercially available Prestone® Ready to Use Premixed Anti-freeze) at 125°C for up to 3000 hours (500 hour intervals). One set of 5 samples for each formulation is removed from the test fluid at 500 hour intervals, washed with water, wiped dry and its tensile properties tested. Resistance to hydrolysis is demonstrated by comparing the tensile properties of the treated bars with
20 untreated bars.

While various embodiments of methods of production of compositions, and methods of use of the compositions have been described in considerable detail herein, the embodiments are merely offered by way of non-limiting examples of the invention described herein. Many variations and modifications of the embodiments described herein will be
25 apparent in light of the disclosure. It will therefore be understood that various changes and modifications may be made, and equivalents may be substituted for elements thereof, without departing from the scope of the invention. Indeed, this disclosure is not intended to be exhaustive or to limit the scope of the invention. The scope of the invention is to be defined by the appended claims, and by their equivalents.

30 Further, in describing representative embodiments, the disclosure may have presented a method and/or process as a particular sequence of steps. However, to the extent that the method or process does not rely on the particular order of steps set forth herein, the method or process should not be limited to the particular sequence of steps described. It will be appreciated that other sequences of steps may be possible. Therefore, the particular order of

the steps disclosed herein should not be construed as limitations on the claims. In addition, the claims directed to a method and/or process should not be limited to the performance of their steps in the order written, and it will be readily appreciated that the sequences may be varied and still remain within the spirit and scope of the present invention.

- 5 It is therefore intended that the invention will include, and this description and the appended claims will encompass, all modifications and changes apparent based on this disclosure.

WHAT IS CLAIMED IS:

1. A thermoplastic pelletizable polymer composition comprising:
 - (a) a polyamide; and
 - (b) a polymer polymerized from maleic anhydride and an olefin selected from the group consisting of ethylene, propylene, isobutylene, butene-1, octene, butadiene, isoprene, hexene, dodecene, dodecene-1, and tetradecene; wherein the polyamide and the polymer are compounded.
2. The thermoplastic pelletizable polymer composition of claim 1 wherein the polyamide is selected from the group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, nylon-9, nylon-10, nylon-11, nylon-12, nylon 6-10, aromatic polyamides, elastomeric polyamides, and mixtures thereof.
3. The thermoplastic pelletizable polymer composition of claim 2 wherein the polyamide is selected from the group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, and mixtures thereof.
4. The thermoplastic pelletizable polymer composition of claim 1 wherein the olefin is selected from the group consisting of ethylene, propylene, and isobutylene.
5. The thermoplastic pelletizable polymer composition of claim 1 wherein the olefin is ethylene.
6. A cross-linked polymer composition comprising:
 - (a) a polyamide, and
 - (b) a polymer polymerized from maleic anhydride and an olefin selected from the group consisting of ethylene, propylene, isobutylene, butene-1, octene, butadiene, isoprene, hexene, dodecene, dodecene-1, and tetradecene; wherein the polyamide and the polymer are compounded at a processing temperature wherein the processing temperature is sufficient to promote cross-linking.
7. The cross-linked polymer composition of claim 6 wherein the polyamide is selected from the group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, nylon-9, nylon-10, nylon-11, nylon-12, nylon 6-10, aromatic polyamides, elastomeric polyamides, and mixtures thereof.
8. The cross-linked polymer composition of claim 6 wherein the polyamide is selected from the group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, nylon-11, and mixtures thereof.
9. The cross-linked polymer composition of claim 6 wherein the olefin is selected from the group consisting of ethylene, propylene, and isobutylene.
10. The cross-linked polymer composition of claim 6 wherein the olefin is ethylene.

11. A method of preparing a compounded polyamide comprising:
compounding a polyamide mixture comprising a polyamide and an
olefin-maleic anhydride copolymer, wherein the olefin is selected from the group consisting of
ethylene, propylene, isobutylene, butene-1, octene, butadiene, isoprene, hexene, dodecene,
5 dodecene-1, and tetradecene, at a processing temperature.
12. The method of claim 11, wherein the olefin is selected from the group
consisting of ethylene, propylene, and isobutylene.
13. The method of claim 11 wherein the olefin is ethylene.
14. The method of claim 11, wherein the polyamide is a nylon.
- 10 15. The method of claim 11 wherein the polyamide is selected from the
group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, nylon-9, nylon-
10, nylon-11, nylon-12, nylon 6-10, aromatic polyamides, elastomeric polyamides, and
mixtures thereof.
- 15 16. The method of claim 11 wherein the polyamide is selected from the
group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, and mixtures
thereof.
17. The method of claim 13, wherein the olefin-maleic anhydride copolymer
has a ratio of ethylene to maleic anhydride of 1:1.
18. The method of claim 17, wherein the olefin-maleic anhydride copolymer
20 has a molecular weight of about 300 to 1,000,000.
19. The method of claim 17, wherein the olefin-maleic anhydride copolymer
has a concentration of about 0.01% to about 0.5%, about 0.5% to about 1.0%, about 1.0% to
about 1.5%, or 1.5% to about 3.0% w/w.
20. The method of claim 11, wherein the processing temperature is about
25 230°C to about 300°C.
21. The method of claim 11, wherein the polyamide mixture further
comprises a glass fiber.
22. The method of claim 21, wherein the glass fiber has a concentration of
about 0.1% to about 30%
- 30 23. The method of claim 11, wherein the polyamide mixture further
comprises one or more stabilizing agents.
24. The method of claim 23, wherein each of the one or more stabilizing
agents is independently selected from a group consisting of cuprous iodide, potassium iodide,
tris (2,4-di-tert-butylphenyl)phosphite, and N,N'-hexane-1,6-diylbis(3-(3,5-di-tert-butyl-4-
35 hydroxyphenyl)propionamide)).

25. The method of claim 23, wherein each of the one or more stabilizing agents independently has a concentration of about 0.01 to about 1.0% w/w.

26. A method of producing a compounded polyamide, comprising compounding a polyamide mixture, where the polyamide mixture comprises an olefin-maleic anhydride copolymer with the olefin selected from the group consisting of ethylene, propylene, isobutylene, butene-1, octene, butadiene, isoprene, hexene, dodecene, dodecene-1, and tetradecene; a glass fiber and; one or more stabilizing agents at a temperature of between about 230°C and about 300°C .

27. A compounded polyamide produced by a process comprising compounding a polyamide mixture, comprising a polyamide and an olefin-maleic anhydride copolymer, wherein the olefin is selected from the group consisting of ethylene, propylene, and isobutylene at a processing temperature.

28. The compounded polyamide of claim 27 wherein the olefin-maleic anhydride polymer is an ethylene-maleic anhydride polymer.

29. The compounded polyamide of claim 27, wherein the polyamide is selected from the group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, nylon-9, nylon-10, nylon-11, nylon-12, nylon 6-10, aromatic polyamides, elastomeric polyamides, and mixtures thereof.

30. The compounded polyamide of claim 27 wherein the polyamide is selected from the group consisting of nylon-6, nylon 6-6, a copolymer of nylon-6 and nylon 6-6, and mixtures thereof.

31. The compounded polyamide of claim 27, wherein the polyamide is selected from a group consisting of nylon-6 and nylon 6-6.

32. The compounded polyamide of claim 28, wherein the ethylene maleic anhydride copolymer has a ratio of ethylene to maleic anhydride of 1:1.

33. The compounded polyamide of claim 28, wherein the ethylene-maleic anhydride copolymer has a molecular weight of about 300 to 1,000,000.

34. The compounded polyamide of claim 27, wherein the ethylene-maleic anhydride has a concentration of about 0.01% to about 0.5%, about 0.5% to about 1.0%, about 1.0% to about 1.5%, or 1.5% to about 3.0% w/w.

35. The compounded polyamide of claim 27, wherein the processing temperature is from about 230°C to about 300°C.

36. The compounded polyamide of claim 27, wherein the polyamide mixture further comprises a glass fiber.

37. The compounded polyamide of claim 36, wherein the glass fiber has a concentration of about 0.1% to about 30%.

38. The compounded polyamide of claim 27, wherein the polyamide mixture further comprises one or more stabilizing agents.

39. The compounded polyamide of claim 38, wherein the one or more stabilizing agents are each independently selected from the group consisting of cuprous iodide, potassium iodide, tris (2,4-di-tertbutylphenyl)phosphite, and N,N'-hexane-1,6-diylbis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionamide)).

40. The compounded polyamide of claim 39, wherein the one or more stabilizing agents each independently has a concentration of about 0.01 % w/w to about 1.0% w/w.

41. The compounded polyamide of claim 33, wherein the ethylene maleic anhydride copolymer has a molecular weight of about 60,000 to about 400,000.

42. The compounded polyamide of claim 13, wherein the ethylene maleic anhydride copolymer has a molecular weight of about 60,000 to about 400,000.

43. The compounded polyamide or polymer composite of any one of the preceding claims wherein the polyamide is a recycled nylon.

44. An article comprising the compounded polyamide or the polymer composite of any one of claims 1 to 42, wherein the article is selected from the group consisting of carpet fiber, apparel, an airbag, a tire, a rope, a conveyer belt, a hose, luggage, a molded auto part, a molded gun frame, a molded electrical part, a molded tool handle, toothbrush, a comb, a hairbrush, a food packaging film, an oil-resistant gasket, and bullet-resistant materials.