

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(10) International Publication Number  
**WO 2013/071474 A1**

(43) International Publication Date  
23 May 2013 (23.05.2013)

(51) International Patent Classification:

**B29C 45/00** (2006.01)    **C08K 5/00** (2006.01)  
**B65D 63/10** (2006.01)    **C08L 77/00** (2006.01)  
**C08K 3/00** (2006.01)

(21) International Application Number:

PCT/CN2011/082153

(22) International Filing Date:

14 November 2011 (14.11.2011)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicant (for all designated States except US): **HONEYWELL INTERNATIONAL INC.** [US/US]; 101 Columbia Road, Morristown, New Jersey 07962 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **HUANG, Jianfeng** [CN/CN]; 18-201, Shangpu Rd. 329, Pudong, Shanghai 200124 (CN). **YUAN, William** [CN/CN]; 430 Li Bing Road, Shanghai 201203 (CN). **WANG, Lei** [CN/CN]; #54-801, 4333 Zhenbei Road, Shanghai 200000 (CN). **PENG, Shuwen** [CN/CN]; Room 201, No 68, Lane 459, East Boshan Road, Pudong, Shanghai 200135 (CN). **WEI, Jie** [CN/CN]; 430 Li Bing Road, Zhang Jiang Hi-Tech Park Pudong New Area, Shanghai 201203 (CN).

(74) Agent: **CHINA PATENT AGENT (H. K) LTD.**; 22/ F, Great Eagle Centre, 23 Harbour Road, Wanchai, Hong Kong (CN).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))



**WO 2013/071474 A1**

(54) Title: POLYAMIDE COMPOSITION FOR LOW TEMPERATURE APPLICATIONS

(57) Abstract: A polyamide composition is formed from a low viscosity polyamide-6 and a nucleating agent. The nucleating agent includes an organic material, a first inorganic material and a second inorganic material. Suitable organic materials include organic polymers. Suitable inorganic metallic materials include metal oxides and silicates. Cable ties and methods of molding cable ties from the polyamide composition are also provided.

## POLYAMIDE COMPOSITION FOR LOW TEMPERATURE APPLICATIONS

## FIELD OF THE INVENTION

**[0001]** The present invention is generally related to the field of polyamides. In particular, the present invention is related to polyamide compositions formed from polyamide-6 and a combination of nucleating agents, and methods of making articles from such polyamide compositions.

## DESCRIPTION OF RELATED ART

**[0002]** Stable low molecular weight and low viscosity polyamides, such as polyamide-6 and polyamide-66, are used for a variety applications including for engineering plastics and textile applications. In the area of engineering plastics, these polyamides may be used in applications utilizing injection molding techniques.

**[0003]** The relative properties and performance characteristics of polyamide-6 and polyamide-66 make each polymer more suitable for certain applications. For example, cable ties used in the auto and electronics industries have historically been manufactured from polyamide-66 using an injection molding process to meet industry performance requirements. Although polyamide-6 offers certain benefits over polyamide-66 for manufacturing cable ties, issues with poor mold release, breakage and brittleness have impeded the manufacture of cable ties from polyamide-6.

## SUMMARY OF THE INVENTION

**[0004]** One embodiment of the invention is a cable tie comprising an elongated polymer body formed from a polyamide composition. The polyamide composition includes a polyamide-6 material and a nucleating agent. The nucleating agent includes at least one organic material, at least a first inorganic material and at least a second inorganic material. The polyamide composition may also include an amino functional silicone oil and a lubricating agent.

**[0005]** Another embodiment is a method for forming a cable tie from a polyamide composition including at least one polyamide-6 material and a nucleating agent having at least one organic material, at least a first inorganic material and at least a second inorganic material. The polyamide composition is melted, injected

into a mold, and cooled to form the cable tie. The cable tie is then released from the mold.

#### BRIEF DESCRIPTION OF THE FIGURES

**[0006]** FIG. 1 is a flowchart illustrating a method of forming a polyamide composition according to embodiments of the present invention.

**[0007]** FIG. 2 is a flowchart illustrating a method of forming a cable tie according to embodiments of the present invention.

**[0008]** FIG. 3 shows a cable tie manufactured according to embodiments of the present invention.

**[0009]** FIG. 4 is a graphical representation of crystalline structures of several polyamide compositions.

#### DETAILED DESCRIPTION

**[0010]** The present invention relates to polyamide compositions useful for a variety of applications including for the manufacture of cable ties by injection molding processes. In one embodiment, the polyamide composition includes at least one polyamide-6 material, at least one nucleating agent and at least one optional lubricant.

**[0011]** Suitable polyamide-6 materials are generally formed by reacting caprolactam and aminocaproic acid under temperature conditions suitable to initiate polymerization. Different polyamide-6 materials can be produced by changing the reaction time and/or temperature, by the inclusion of catalysts and by forming various end groups on the polyamide-6 material. Examples of commercially available polyamide-6 materials include Aegis<sup>®</sup> brand polyamide-6 products available from Honeywell International Inc. Specific examples of these products are sold under the brand designations H35ZI, H8202NLB, H35L, H50LN and H50L. The polyamide-6 may constitute at least about 90 wt% of the polyamide composition, more particularly, at least about 95 wt% of the polyamide composition. In one embodiment, the polyamide-6 may have a low viscosity, for example, less than about 52 FAV, more particularly, between about 25 and about 42 FAV, and even more particularly, between about 30 FAV and 42 FAV.

**[0012]** Additionally, the polyamide composition may be blended with one or more polyamide-66 compositions if desired. In one embodiment, such a blended composition includes up to about 50 wt% of a polyamide-66 material.

**[0013]** In some embodiments, the nucleating agent may include mixtures of organic and inorganic components. Examples of suitable organic materials include organic salts such as carboxylic acid salts, amides such as arylamides, and organic polymers. Various polyamide materials other than polyamide-6 may be particularly suitable. In particular polyamides having a ratio of carbon atoms to amide groups of less than 5:1, more particularly, less than 3:1, even more particularly, no more than 2:1. An exemplary polyamide is polyamide-22.

**[0014]** Examples of inorganic materials suitable for use in the nucleating agent include inorganic metallic materials. Suitable inorganic metallic materials include metal oxides and metal silicates. Particularly suitable inorganic metallic materials include alumina silicate, aluminum oxide and silicon dioxide. Other suitable inorganic materials include talc, mica, kaolin, asbestos, alumina, silica, silver bromide, graphite, molybdenum disulfide, lithium fluoride, sodium phenylphosphinate, sodium isobutylphosphinate, magnesium oxide, mercuric bromide, mercuric chloride, cadmium acetate, lead acetate, silver chloride and the like.

**[0015]** In some embodiments, the nucleating agent may include at least two inorganic materials. In some embodiments, one of the inorganic materials may be a clay. In some embodiments, the clay may be a nano clay. Nano clays are nanoparticles of layered mineral silicates. Examples of types of nano clays include montmorillonite, bentonite, kaolinite, hectorite and halloysite. In some embodiments, the clay is a montmorillonite, which includes layers of aluminosilicate that are about 1 nanometer thick. In some embodiments, the clay may also include magnesium. In some embodiments, the clay may be an organic modified montmorillonoid clay. In some cases, including an organic ion can help to separate the layers of aluminosilicate.

**[0016]** In some embodiments, at least some of the native sodium and/or calcium ions in the montmorillonoid clay may be replaced with a variety of different ammonium ions. Illustrative examples of suitable organic modifiers include but are not limited to bis(2-hydroxy-ethyl)methyl rapeseed ammonium, bis(2-hydroxy-

ethyl)methyl coco ammonium, bis(2-hydroxy-ethyl)methyl tallow ammonium, trimethyl tallow quaternary ammonium, trimethyl tallow quaternary ammonium, trimethyl hydrogenated-tallow ammonium, trimethyl hydrogenated-tallow ammonium, dimethyl hydrogenated-tallow ammonium, methyl bis(hydrogenated-tallow) ammonium and dimethyl bis(hydrogenated-tallow) ammonium.

**[0017]** Illustrative but non-limiting examples of commercially available organically modified montmorillonoid clay materials include GK-8, having an unknown organic modifier and being available from Jiangxi Gukang of Yichun, Jiangxi China ([www.jxgukang.com](http://www.jxgukang.com)), NANOMER I.34TCN, including bis(2-hydroxy-ethyl)methyl tallow ammonium as organic modifier and being available from Nanocore in the United States ([www.nanocor.com](http://www.nanocor.com)), CLOISITE® 30 B and CLOISITE®93A, both of which are available in the United States from Southern Clay ([www.scprod.com](http://www.scprod.com)). CLOISITE® 30 B includes bis(2-hydroxy-ethyl)methyl tallow ammonium as organic modifier while CLOISITE®93A includes methyl bis(hydrogenated-tallow) ammonium as organic modifier.

**[0018]** In an alternate embodiment, the polyamide composition may include at least one alpha form nucleating agent and at least one gamma form nucleating agent. Polyamide 6 contains two types of stable crystal forms: monoclinic alpha form and monoclinic (or pseudo-hexagonal) gamma form. The crystal structure that forms when polyamide 6 is crystallized from the melt may be influenced by thermal conditions, applied stress, presences of moisture, and additives such as nucleating agents. Alpha form nucleating agents predominantly encourage the formation of alpha form crystals while gamma form nucleating agents predominantly encourage the formation of gamma form crystals. Examples of suitable alpha form nucleating agents include the polyamide nucleating agents discussed herein, and polyamide-22 in particular. Examples of suitable gamma form nucleating agents include the nano clay materials discussed herein, and the montmorillonoid clay materials in particular

**[0019]** By combining an alpha form nucleating and a gamma form nucleating agent, a balanced crystallization rate and toughness can be obtained. As further demonstrated in the examples, this balance may be attributable to the more complex crystal formed by combining the nucleating agents. In one embodiment, the polyamide composition includes sufficient amounts of the gamma form nucleating

agent to produce a polyamide composition that is predominantly gamma crystal form. Compositions containing both the alpha and gamma crystal forms may provide optimal properties for forming cable ties.

**[0020]** The polyamide composition may include less than about 1 wt%

5 nucleating agent, more particularly, less than about 0.5 wt% nucleating agent, and even more particularly between about 0.1 wt% and about 0.3 wt% nucleating agent. In one embodiment, the nucleating agent comprises, consists or consists essentially of a polyamide material such as polyamide-22, a first alumina silicate material and a second alumina silicate material such as montmorillonite. For example, the  
10 nucleating agent may include between about 1 wt% and about 5 wt% alumina silicate, between about 15 wt% and about 30 wt% polyamide such as polyamide-22 and between about 65 wt% and about 85 wt% montmorillonite.

**[0021]** In some embodiments, the nucleating agent may include the organic material, and one of the first or second inorganic materials as a mixture or

15 combination. Particularly suitable combinations of organic and inorganic materials include polyamides having a ratio of carbon atoms to amide groups of less than 5:1 (such as polyamide 2.2) and metal silicates. In one embodiment, the organic component constitutes greater than 50 wt% of the combination, more particularly, between about 60 wt % and about 95 wt %, even more particularly, between about  
20 75 wt% and 90 wt%. The first inorganic component constitutes less than 50 wt% of the combination, more particularly between about 5 wt% and about 40 wt%, even more particularly, between about 5 and about 15 wt%. An exemplary commercially available combination is P22, a 90 wt% polyamide-2.2/10% alumina silicate material manufactured by Brueggemann Chemical.

25 **[0022]** A variety of amino functional silicone oils may be suitable for use with embodiments of the present invention. In some embodiments, amino functional silicones have good compatibility with nylon as a result of the amine groups in the macromolecular chain. Examples of suitable amino functional silicone oils include those available under the XIAMETER<sup>®</sup> name, including XIAMETER<sup>®</sup> OFX-8417,  
30 XIAMETER<sup>®</sup> OFX-8822 and XIAMETER<sup>®</sup> OFX-8468. Further examples of suitable amino functional silicone oils include BD-1007.

**[0023]** A variety of lubricating agents may be suitable for use with embodiments of the present invention. Examples of suitable lubricating agents include stearamides such as ethylene-bis-stearamide, stearates such as zinc stearate, magnesium stearate, calcium stearate, and sodium stearate, glycerol fatty acid esters such as glycerol monostearate, polysiloxanes such as polydimethylsiloxane, polyolefins, and ethylenevinylacetate copolymers. Particularly suitable additives include calcium stearate and/or ethylene-bis-stearamide. The lubricating agent may constitute less than 5 wt% of the polyamide composition, more particularly, less than 2 wt% of the polyamide composition.

**[0024]** Table 1 sets forth exemplary embodiments of the present invention:

TABLE 1

Component	Embodiment 1	Embodiment 2	Embodiment 3
Polyamide-6	90.0-99.5 wt%	97.0-99.5 wt%	97.0-99.0 wt%
Nucleating Agent	0.05 – 1.50 wt%	0.1 – 0.5 wt%	0.1 – 0.3 wt%
Silicone Oil	0.2 – 5 wt%	0.5 – 2 wt%	0.5 – 1.5 wt%
Lubricating Agent	0.05 – 2 wt%	0.1 – 1.5 wt%	0.1 – 1.0 wt%

**[0025]** The polyamide composition may further include a variety of optional additives. Exemplary additives include, but are not limited to: antioxidants, thermal stabilizers, anti-weathering agents, mold releasing agents, pigments, dyes, plasticizers, antistatic agents, flame retardants, glass fillers, mineral fillers and impact modifiers. The polyamide composition may also include a fibrous or particulate filler, which functions to increase the modulus and stiffness of the composition.

**[0026]** The polyamide composition may be formed by conventional procedures. In one embodiment, the various raw materials are blended together. Appropriate blending techniques include melt extrusion, batch melting and the like. In one useful procedure, the blending procedure can be carried out at elevated temperatures above the melting point of the polymer and the nucleating agent either preformed, as individual components of the agent separately, or as a combination of

the components in a suitable form such as granules, pellets and powders added to the melt with vigorous stirring.

**[0027]** Alternatively, all or a portion of the various components of the nucleating agent can be masterbatched or preblended with the polyamide in the melt, and this premixed or masterbatch may be added to the polyamide in the melt in amounts sufficient to provide the desired amount of nucleating agent in the polyamide product. Stirring is continued until a homogeneous composition is formed. Blending temperatures and blending pressures, and the order of addition of the various components may be varied as desired provided that a substantially homogeneous composition results. The blending procedure can be carried out at elevated temperatures, in which case the polymer component is melted and the solid nucleating agents are admixed therewith by vigorously stirring the melt. Similarly, the various solid components can be granulated, and the granulated components mixed dry in a suitable blender, or for example, a Banbury mixer, as uniformly as possible, then melted in an extruder and extruded with cooling.

**[0028]** Fig. 2 illustrates a method 10 of forming a polyamide composition according to embodiments of the present invention. A polyamide mixture is formed by blending the polyamide material, the nucleating agent, the amino functional silicone oil and the lubricating agent (block 20). The mixture is then compounded (block 30) and pelletized (block 40). The pellets are then batch mixed (block 50) and packaged (block 60) in a desired form for future use.

**[0029]** In one embodiment, the polyamide composition is then blended with at least one additional polyamide material such as a polyamide-66 material. The resulting polyamide blend may include from about 5 wt% to about 95 wt% of the polyamide-66 composition, more particularly, from about 10 wt% to about 50 wt% or the polyamide-66 composition.

**[0030]** The resulting polyamide composition may be utilized to manufacture a variety of molded articles, fibers and films. Suitable molding techniques include injection molding, melt spinning, casting and extruding. In a particular embodiment, the polyamide composition may be used to manufacture electronic cable ties by injection molding techniques.



**[0031]** Fig. 3 illustrates a method 100 of forming cable ties according to embodiments of the present invention. A polyamide composition as described above is melted at a suitable temperature, for example between about 250° and 300° C (block 110). The composition is then injected into a suitable mold at an injection pressure that is preferably below about 1000 kgf/cm<sup>2</sup> (block 120). The mold is cooled to solidify the polyamide composition in the form of a cable tie (block 130). The cable tie is then released from the mold (block 140).

**[0032]** Fig. 4 shows an exemplary cable tie 200 according to one embodiment of the present invention. The cable tie 200 includes an elongate body 210, gear teeth 220 and a ratchet 230. In use, the cable tie 200 is wrapped around an object or objects, and the teeth 220 are inserted into the ratchet 230. The ratchet 230 includes a locking mechanism that interfaces with individual gear teeth. Of course, a variety of different cable tie configurations can be manufactured using the polyamide compositions of the present invention.

**[0033]** As set forth in the examples below, cable ties formed from the polyamide compositions of the present invention exhibit improved crystallinity, lower injection pressure, reduced mold sticking and sprue breakage and/or lower brittleness compared to both conventional polyamide-6 and polyamide-66 compositions. As such the polyamide compositions of the present invention are a viable substitute for polyamide-66 for a variety of applications including for forming cable ties.

## EXAMPLES

**[0034]** The present invention is more particularly described in the following examples that are intended as illustrations only, since numerous modifications and variations within the scope of the present invention will be apparent to those skilled in the art. Unless otherwise noted, all parts, percentages, and ratios reported in the following examples are on a weight basis, and all reagents used in the examples were obtained, or are available, from the chemical suppliers described below, or may be synthesized by conventional techniques.

**[0035]** The compositions of Examples 1-4 and Comparative Examples A-E set forth in Table 2 below were master-batched by tumble blending the ingredients, and

feeding the tumbled ingredients into the throat of a twin screw extruder (lab size 30 mm diameters) utilizing standard lab practices. H35ZI is a polyamide-6 composition available from Honeywell International Inc. MMT is an organic modified montmorillonoid clay nucleating agent available from Jiangxi Gukang of Yichun, Jiangxi China as GK-8. P22 is a nucleating agent available from Bruggemann Chemical that constitutes a 90 wt% polyamide-2.2/10 wt% alumina silicate mixture. CaV102 is a nucleating agent and stands for Licomont® CaV102, which is a calcium salt of montanic acid, which is a long chain saturated linear carboxylic acid.

**[0036]** ASO BD-1007 is an amino functional silicone. ZnSt is zinc stearate and is an external lubricant. CaSt is calcium stearate and is an external lubricant. GMS is glycerol monostearate and is an internal lubricant. EBS is N/N'-ethylene bis-stearamide, an internal lubricant. PA66 21SPC is a commercial PA66 for cable tie applications.

TABLE 2

Component	H35ZI	MMT	P22	CaV102	ASO BD-1007	ZnSt	CaSt	GMS	EBS	PA66 21SPC
Example										
1	98.3	0.15	0.05		1				0.5	
2	98.3	0.1	0.1		1				0.5	
3	98.3	0.05	0.15		1				0.5	
4	97.4	0.15	0.05		1		0.5	0.5	0.4	
Comp Ex.										
A	98.3	0.2			1				0.5	
B	97.73		0.2		1	0.97			0.1	
C	98.3	0.15		0.05	1				0.5	
D	98.3	0.05		0.15	1				0.5	
E										100

**[0037]** Compositions 1-4 and Comparative Examples A-E were injection-molded to form cable ties for testing purposes. As shown below in Table 3, the table

ties were subjected to a bend test under several different conditions as well as a fall hammer impact test. In the bend test (dry molded), a cable tie is bent 180 degrees and the fracture number is recorded. In the bend test (cold conditioned), the cable tie is subjected to a temperature of -40 °C for 2 hours before being bent 180 degrees as before. In the bend test (warm aged), the cable tie is dried at 80 °C for 24 hours as before. After being at room temperature for 20 minutes, the cable tie is bent 180 degrees as before. In the fall hammer impact test, the cable tie is installed on a steel mandrel and is placed at -40 °C for 2 hours. The sample is then placed on a V block and a free fall hammer impacts the strap ten seconds after removal of the test assembly from the freezer.

TABLE 3

Example	1	2	3	4	A	B	C	D	E
Injection molding temperature	285 °C								
Injection Pressure (kgf/cm <sup>2</sup> )	1075	1050	1050	950	1050	1100	1075	1075	1400
Bend Test (# in 10)	dry molded	0	0	0	0	0	0	0	0
	cold conditioned	2	2	4	2	10	0	10	10
	warm aged	0	0	0	0	0	10	2	2
Fall hammer test	2	0	1	0	0	0	1	3	1

**[0038]** As can be seen, Comparative Example A (MMT only) performed poorly at cold temperatures, with all ten samples breaking. Comparative Example B (P22 only) performed poorly in the warm aging test, with all ten samples breaking. In Comparative Examples C and D, MMT was paired with CaV102, which performed poorly at cold temperatures, with all ten samples of each breaking. Note that the commercial PA66 material required a higher melt temperature and injection pressure for processing.

**[0039]** With respect to Examples 1-4, it can be seen that Examples 2 and 4 performed better than Examples 1 and 3. In Example 2, the relative amounts of

MMT and P22 were equal. In Example 4, there was a 3 to 1 ratio of MMT to P22. Example 1 also had a 3 to 1 ratio of MMT to P22, but lacked the calcium stearate and glyceryl monostearate included in Example 4. Example 3 had a 1 to 3 ratio of MMT to P22.

- 5 **[0040]** The compositions of Examples 1 and 5-7 and Comparative Examples F-I are set forth in Table 4 below. Examples 1 and 5-7 have the same MMT to P22 ratio, but include differing amino silicone oils. ASO OFX-8417 is XIAMETER<sup>®</sup> OFX-8417, an amino functional silicone. ASO OFX-8822 is XIAMETER<sup>®</sup> OFX-8822, an amino functional silicone. ASO OFX-8468 is XIAMETER<sup>®</sup> OFX-8468, an amino  
 10 functional silicone. ESO BD-1208 is an epoxy functional silicone. N-BBSA is n-butyl benzene sulfonamide.

TABLE 4

	H35ZI	MMT	P22	ASO BD- 1007	ASO OFX- 8417	ASO OFX- 8822	ASO OFX- 8468	ESO BD- 1208	N- BBSA	ZnSt	EBS
Example											
1	98.3	0.15	0.05	1							0.5
5	98.3	0.15	0.05		1						0.5
6	98.3	0.15	0.05			1					0.5
7	98.3	0.15	0.05				1				0.5
Comp Ex											
F	98.73		0.2							0.97	0.1
G	98.63	0.3								0.97	0.1
H	97.73		0.2					1		0.97	0.1
I	98.3	0.2							1		0.5

- 15 **[0041]** These compositions were tested as before. The test results are summarized below in Table 5.

TABLE 5

Example	1	5	6	7	F	G	H	I	
Injection molding temperature	285 °C								
Injection Pressure (kgf/cm <sup>2</sup> )	1075	1150	1150	1150	1100	950	950	1075	
Bend Test (# in 10)	dry molded	0	0	0	2	0	10	5	5
	cold conditioned	2	2	5	4	8	10	9	10
	warm aged	0	1	0	0	6	10	7	10
	Fall hammer test	2	0	1	1	0	10	6	3

**[0042]** Examples 1 and 5-7 illustrate the use of different grades of amino functional silicone. Examples 1 and 5 outperformed Examples 6 and 7. Comparative Examples F and G lacked an amino functional silicone and performed poorly.

- 5 Comparative Example H illustrated that an epoxy functional silicone does not work. Comparative Example I illustrated that a plasticizer for polyamide does not work.

#### Example Eight

**[0043]** Non-isothermal analyses were carried out using a differential scanning calorimeter thermal analyzer (DSC). Each sample was heated from 25 °C to 280 °C at a rate of 50 Kelvin (K) per minute. The 280 °C temperature was maintained for two minutes and the samples were then cooled back to 25 °C at varying rate of 2.5 K/min, 5 K/min, 10 K/min, 20 K/min and 40 K/min. The test data was analyzed using Mo Zhishen's method (see *Qiao XY, Wang XH, Zhao XJ, Mo ZS, Zhang HF (2000) Synthetic Met 113.1*).

**[0044]** The Crystallization data is summarized below in Table 6. The PA6 containing MMT has a lower necessary cooling rate "F(t)" to achieve a defined degree of crystallinity at a particular unit time "X(t)" than the PA6 containing P22. The lower F(t) value indicates a faster crystallization rate. The alpha value in Table 6 is a ratio of an Avrami index (used in isothermal crystallization kinetic studies) and an Ozawa index (used in non-isothermal crystallization kinetic studies). As can be seen, the PA6, the PA6 (MMT) and PA6 (P22) have a relatively constant alpha value. In contrast, the PA6 (MMT and P22) has a variable alpha value, indicating that the crystallization mechanism is complex.

TABLE 6

X(t), %	PA6		PA6 (0.3% MMT)		PA6 (0.2% P22)		PA6 (0.15% MMT + 0.05% P22)	
	F(T)	alpha	F(T)	alpha	F(T)	alpha	F(T)	alpha
20	6.92	1.85	3.1	1.35	3.14	1.4	5.95	0.87
40	10.23	1.76	4.21	1.37	4.59	1.41	6.91	0.92
60	13.35	1.72	5.66	1.44	6.65	1.45	8.29	0.99
80	18.12	1.71	9.95	1.51	12.24	1.42	11.57	1.12
90	24.62	1.74	19.56	1.46	22.14	1.32	18.68	1.27

**[0045]** Differences in crystal form using a combination of MMT and P22 as a nucleating agent was also observed using wide angle X ray diffraction. Figure 4 is a graphical representation of intensity, in which the relative intensity (height) is an indication of the relative amounts of the alpha and gamma crystal forms present in two PA6 compositions. Notably, PA6 containing MMT includes only the gamma crystal form. PA6 containing P22 includes both alpha and gamma forms, but the alpha form is predominant. The alpha and gamma forms also coexist in the PA6 having both P22 and MMT nucleating agents, but Figure 4 indicates that the gamma form is predominant.

**[0046]** The examples indicate that PA6 with MMT is more brittle than PA6 with P22, but has a higher crystallization rate. By combining MMT and P22 as a nucleating agent, a balanced crystallization rate and toughness can be obtained. This balance may be attributable to the more complex crystal formed by combining the nucleating agents.

**[0047]** From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

## CLAIMS

1. A cable tie comprising:

an elongate polymer body having a first end and a second end, the elongate polymer body comprising a polyamide composition, wherein the polyamide  
5 composition comprises at least one polyamide-6 material and a nucleating agent, the nucleating agent comprising at least one organic material and at least first and second inorganic materials.

2. The cable tie of claim 1, wherein the organic material comprises a polymer.

3. The cable tie of claim 1, wherein the organic material comprises a polyamide  
10 having a ratio of carbon atoms to amide groups of less than 5:1.

4. The cable tie of claim 1, wherein the organic material comprises a polyamide having a ratio of carbon atoms to amide groups of no more than 2:1.

5. The cable tie of claim 1, wherein the organic material comprises polyamide-22.

6. The cable tie of claim 1, wherein the first or second inorganic material  
15 comprises a metal oxide, a silicon dioxide or a derivative or combination thereof.

7. The cable tie of claim 1, wherein the first or second inorganic material comprises a metal silicate.

8. The cable tie of claim 1, wherein the first or second inorganic material comprises alumina silicate.

20 9. The cable tie of claim 1, wherein the first or second inorganic material comprises a nano clay.

10. The cable tie of claim 1, wherein the first or second inorganic material comprises montmorillonite, bentonite, kaolinite, hectorite or halloysite.

25 11. The cable tie of claim 1, wherein the first or second inorganic material comprises an organically modified montmorillonoid clay.

12. The cable tie of claim 1, wherein the first inorganic material comprises alumina silicate and the second inorganic material comprises an organically modified montmorillonoid clay.
13. The cable tie of claim 1, wherein the at least one organic material and the first  
5 inorganic material comprises a mixture of a polyamide material having a ratio of carbon atoms to amide groups of less than 5:1 and alumina silicate.
14. The cable tie of claim 1, wherein the polyamide composition comprises less than 0.5 wt% nucleating agent.
15. The cable tie of claim 1, wherein the polyamide composition further comprises  
10 at least one polyamide-66 material.
16. The cable tie of claim 1, wherein the polyamide composition further comprises at least one stearate, stearamide, polysiloxane, polyolefin, ethylenevinylacetate copolymer or combination thereof.
17. The cable tie of claim 1, wherein the polyamide composition comprises  
15 ethylene-bis-stearamide, zinc stearate, magnesium stearate, calcium stearate, sodium stearate, glycerol monostearate, polydimethylsiloxane, polyolefin, and ethylenevinylacetate copolymers or combinations thereof.
18. The cable tie of claim 1, wherein the polyamide composition comprises one or both of a stearamide and a stearate.
- 20 19. The cable tie of claim 1, wherein the polyamide composition comprises one or more of ethylene-bis-stearamide, calcium stearate and glycerol monostearate.
20. The cable tie of claim 1, wherein the polyamide composition comprises a polyamide-66 material.
21. A polyamide composition comprising:
- 25 a polyamide-6 material;
- at least one additional polyamide material;



alumina silicate; and

an organically modified montmorillonoid clay.

22. The polyamide composition of claim 21, further comprising a lubricant.

23. The polyamide composition of claim 21, further comprising an amino silicone  
5 oil.

24. The polyamide composition of claim 21 wherein the at least one additional polyamide material comprises polyamide-22.

25. The polyamide composition of claim 21 wherein the at least one additional polyamide material comprises polyamide-66.

10 26. The polyamide composition of claim 21, wherein the organically modified montmorillonoid clay comprises a quaternary ammonium organic modifier.

27. A method for forming a cable tie comprising:

melting a polyamide composition comprising at least one polyamide-6 material and a nucleating agent, the nucleating agent comprising at least one  
15 organic material and at least first and second inorganic materials;

injecting the melted polyamide composition into a mold;

cooling the mold to form a cable tie; and

releasing the cable tie from the mold.

28. The method of claim 27, wherein the polyamide composition is melted at a  
20 temperature of less than 300 °C.

29. The method of claim 27, wherein the polyamide composition is injected at a pressure of less than 1000 kgf/cm<sup>2</sup>.

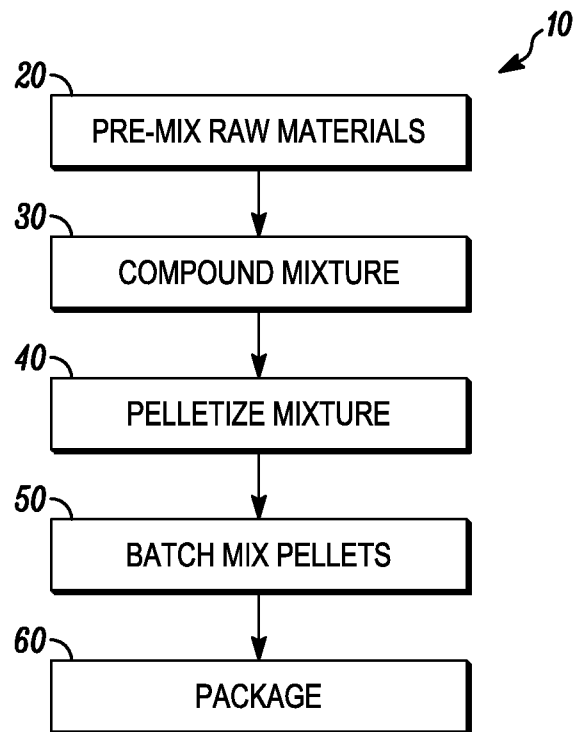
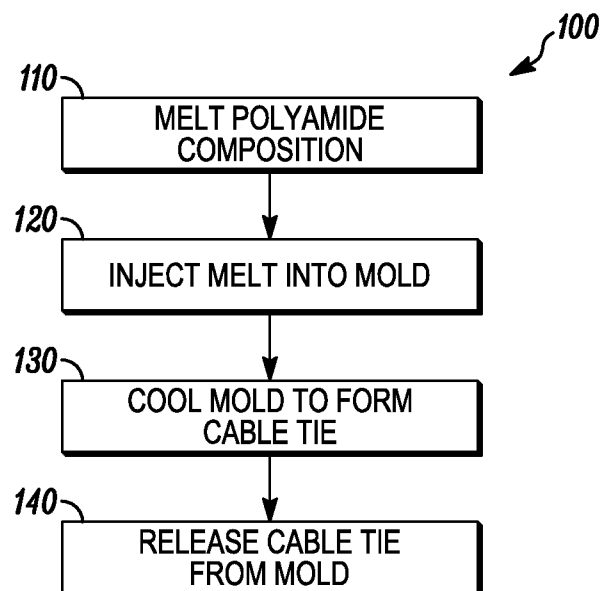
30. The method of claim 27 wherein the polyamide composition is combined with a polyamide-66 material prior to the injecting step to form a polyamide blend.

31. The method of claim 30 wherein the polyamide blend comprises from about 1 wt% to about 50 wt% of the polyamide composition.

32. A cable tie comprising:

an elongate polymer body having a first end and a second end, the elongate polymer  
5 body comprising a polyamide composition, wherein the polyamide composition  
comprises at least one polyamide-6 material, at least one alpha form nucleating  
agent, and at least one gamma form nucleating agent, wherein the crystal form of  
the polymer composition is predominantly the gamma form.

33. The elongate polymer body of claim 32 wherein the at least one alpha form  
10 nucleating agent comprises a polyamide material and the at least one gamma form  
nucleating agent comprises a montmorillonoid clay.

*FIG. 1**FIG. 2*

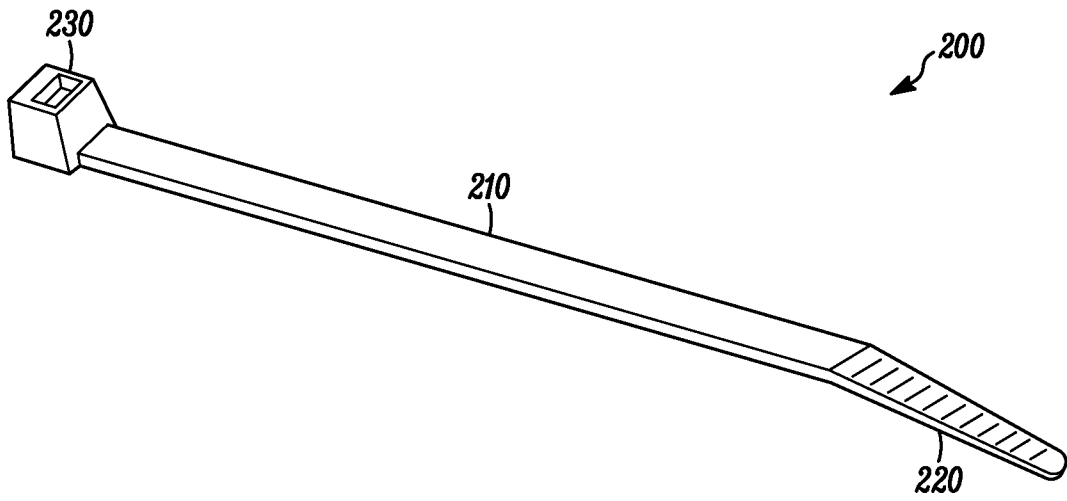


FIG. 3

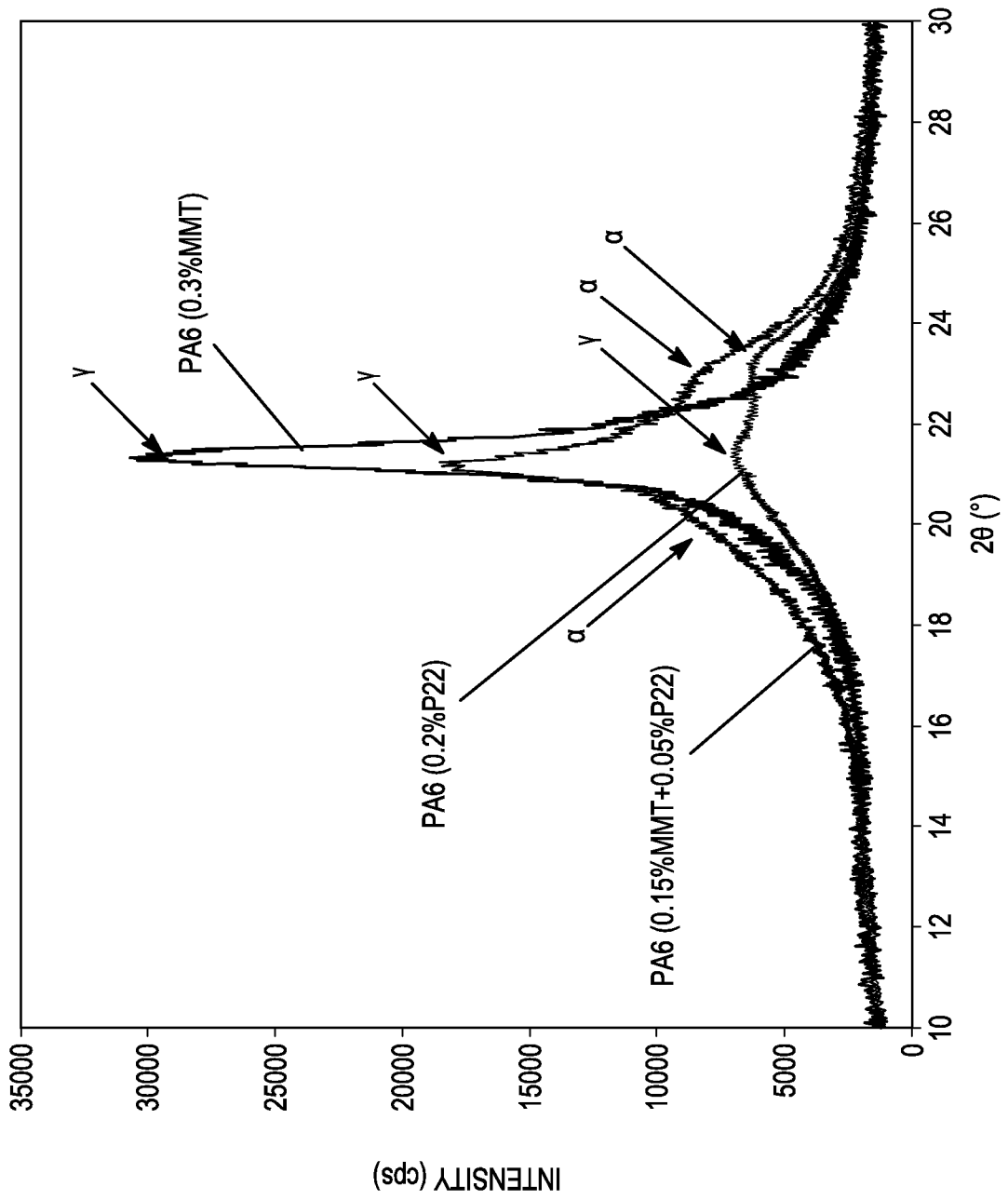


FIG. 4

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/CN2011/082153

## A. CLASSIFICATION OF SUBJECT MATTER

See the extra sheet

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: B29C45/-; B65D63/-; C08K3/-; C08K5/-; C08L77/-

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

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

Database: WPI, EPODOC, CPRS, CNKI

Cable tie, polyamide or nylon, nucleating agent, alumina silicate, montmorillonite, clay,

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN101407631 A(SELEN SCI& TECHNOLOGY SHENZHEN CO LTD) 15 April 2009 (15.04.2009) the whole document	1-33
A	CN101899208 A(WUXI HONGGUANG SIGNBOARD CO LTD) 01 Dec. 2010 (01.12.2010) the whole document	1-33
A	CN101899211 A(CHEN Y) 01 Dec. 2010 (01.12.2010) the whole document	1-33
A	WO2011000763 A1(RHODIA OPERATIONS) 06 Jan. 2011(06.01.2011) the whole document	1-33
A	JP2011116841 A(TOYOBO KK) 16 June 2011(16.06.2011) the whole document	1-33
E	WO2012027863A1(HONEYWELL INT INC) 08 Mar. 2012(08.03.2012) the whole document	1-33

Further documents are listed in the continuation of Box C.

See patent family annex.

<p>* Special categories of cited documents:</p> <p>“A” document defining the general state of the art which is not considered to be of particular relevance</p> <p>“E” earlier application or patent but published on or after the international filing date</p> <p>“L” document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>“O” document referring to an oral disclosure, use, exhibition or other means</p> <p>“P” document published prior to the international filing date but later than the priority date claimed</p>	<p>“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>“&amp;”document member of the same patent family</p>
--	--

Date of the actual completion of the international search  
06 Aug. 2012(06.08.2012)

Date of mailing of the international search report  
**16 Aug. 2012 (16.08.2012)**

Name and mailing address of the ISA/CN  
The State Intellectual Property Office, the P.R.China  
6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China  
100088  
Facsimile No. 86-10-62019451

Authorized officer  
**TANG Shaohua**  
Telephone No. (86-10)62084439

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
PCT/CN2011/082153

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN101407631 A	15.04.2009	CN101407631B	19.10.2011
CN101899208 A	01.12.2010	none	
CN101899211A	01.12.2010	none	
WO2011000763 A1	06.01.2011	FR2947556A	07.01.2011
		FR2947556 B1	15.07.2011
		EP2448997 A1	09.05.2012
JP2011116841 A	16.06.2011	none	
WO2012027863A1	08.03.2012	none	

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/082153

## CLASSIFICATION OF SUBJECT MATTER:

B29C45/00 (2006.01)i  
B65D63/10 (2006.01)i  
C08K3/00 (2006.01)i  
C08K5/00 (2006.01)i  
C08L77/00 (2006.01)i