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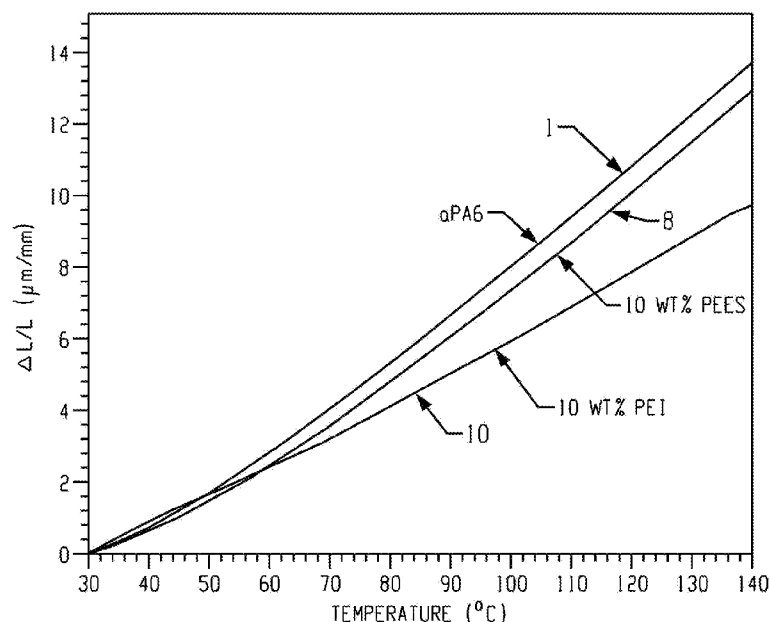


Fig. 9

(57) Abstract: In an embodiment, a polyamide composition comprises an anionically polymerized polyamide; and a thermoplastic polymer. In another embodiment, a method of making a polyamide composition comprises anionically polymerizing a monomer mixture comprising a cyclic lactam monomer, a thermoplastic polymer, a catalyst, and an activator to form the polyamide composition. The Hildebrand solubility factor of the anionically polymerized polyamide can be within 15% of the Hildebrand solubility factor of the thermoplastic polymer.



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POLYAMIDE COMPOSITIONS COMPRISING A THERMOPLASTIC POLYMER

BACKGROUND

[0001] Polyamides are widely known for their high impact resistance, good toughness, abrasion resistance, and strength, where the crystallinity and crystal structure play an important role in determining these properties. Commercially, polyamides are generally synthesized by the ring-opening polymerization of a cyclic lactam monomer, such as ϵ -caprolactam, by hydrolysis, a process requiring multiple steps, making the hydrolysis method unsuitable for injection molding. Conversely, anionic polymerization of cyclic lactam monomers can be very effective for reaction injection molding due to the fast reaction kinetics of the polymerization and the formation of little to no by-products. However, one of the major problems in the formation of polyamides using anionic polymerization is post-mold shrinkage, as such shrinkage can result in dimensional instability, for example, by as much as 10 to 20% and can ultimately result in article failure. While several methods have been considered to reduce the shrinkage of anionically polymerized polyamides, they generally include a melt mixing step, which results in a reduction in the crystallinity of the polyamide and ultimately in a reduction of the mechanical properties.

[0002] Therefore, an improved method of forming a polyamide composition having reduced shrinkage is desired.

BRIEF SUMMARY

[0003] Disclosed herein is a polyamide composition comprising a thermoplastic polymer and a method of making the same.

[0004] In an embodiment, a polyamide composition comprises an anionically polymerized polyamide; and a thermoplastic polymer. A Hildebrand solubility factor of the anionically polymerized polyamide can be within 15% of a Hildebrand solubility factor of the thermoplastic polymer.

[0005] In another embodiment, a method of making a polyamide composition comprises anionically polymerizing a monomer mixture comprising a cyclic lactam monomer, a thermoplastic polymer, a catalyst, and an activator to form the polyamide composition.

[0006] The above described and other features are exemplified by the following figures, detailed description, and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Refer now to the figures, which are exemplary embodiments, and wherein the like elements are numbered alike.

[0008] FIG. 1 is a scanning electron microscopy image of the composition of Example 2;

[0009] FIG. 2 is a scanning electron microscopy image of the composition of Example 4;

[0010] FIG. 3 is a scanning electron microscopy image of the composition of Example 7;

[0011] FIG. 4 is a scanning electron microscopy image of the composition of Example 10;

[0012] FIG. 5 is a graphical illustration of the differential scanning calorimetry scans of Examples 1, 7, 8, and 9;

[0013] FIG. 6 is a graphical illustration of the differential scanning calorimetry scans of Examples 1, 10, 11, and 12;

[0014] FIG. 7 is a graphical illustration of the thermogravimetric analysis of Examples 1, 7, 8, and 9;

[0015] FIG. 8 is a graphical illustration of the thermogravimetric analysis of Examples 1, 10, 11, and 12; and

[0016] FIG. 9 is a graphical illustration of the linear expansion of Examples 1, 8, and 10 with temperature.

DETAILED DESCRIPTION

[0017] During the anionic polymerization of cyclic lactam monomers to form polyamide, there is a significant amount of shrinkage that occurs. This shrinkage arises not only from the inherent densification due to the formation of covalent bonds between the monomers, but also to the fact that the polymerization is generally performed at or below the crystallization temperature of polyamide, so the material crystallizes as it polymerizes and also from thermal contraction of the polyamide during post-polymerization cooling. It was surprisingly discovered that if the cyclic lactam monomers were polymerized in the presence

of a thermoplastic polymer that a reduced shrinkage can be observed in the resulting polyamide composition as compared to a polyamide composition formed under the same reaction conditions but without the presence of the thermoplastic polymer. Specifically, the method comprises anionically polymerizing a monomer mixture comprising a cyclic lactam monomer, the thermoplastic polymer, a catalyst, and an activator to form the polyamide composition.

[0018] A Hildebrand solubility factor of the anionically polymerized polyamide can be within 10%, or within 5% of a Hildebrand solubility factor of the thermoplastic polymer. For example, if the anionically polymerized polyamide comprises polyamide 6 having a Hildebrand solubility parameter of 22.5 Joules to the 1/2 times centimeters to the - 3/2 ($\text{J}^{1/2}\text{cm}^{-3/2}$), then the Hildebrand solubility parameter of the thermoplastic polymer can be 20.2 to 24.8 $\text{J}^{1/2}\text{cm}^{-3/2}$, or 21.3 to 23.6 $\text{J}^{1/2}\text{cm}^{-3/2}$. A Hildebrand solubility factor of the anionically polymerized polyamide can be within 30%, or within 15% of a Hildebrand solubility factor of the thermoplastic polymer. The Hildebrand solubility factor of the thermoplastic polymer and the anionically polymerized polyamide can each independently be greater than or equal to 19 $\text{J}^{1/2}\text{cm}^{-3/2}$, or greater than or equal to 20 $\text{J}^{1/2}\text{cm}^{-3/2}$, or 19 to 25 $\text{J}^{1/2}\text{cm}^{-3/2}$, or 20 to 24 $\text{J}^{1/2}\text{cm}^{-3/2}$. The thermoplastic polymer can be free of (such that it can include 0 to 0.01 wt%) of a poly(methyl methacrylate) having a Hildebrand solubility factor of 18.6 $\text{J}^{1/2}\text{cm}^{-3/2}$.

[0019] While it is not required to provide a description of the theory of operation of the disclosure and the appended claims should not be limited by statements regarding such theory, it is believed that this phase compatibility can result in an improvement in the thermal stability as well as in an improvement in the dimensional stability by lowering the coefficient of thermal expansion of the resultant polyamide composition. If the thermoplastic polymer has a Hildebrand solubility factor that is significantly different from that of the anionically polymerized polyamide, then the polyamide composition can display phase separation. For example, while polystyrene can be considered miscible in some cyclic lactam monomers, the solubility of the polystyrene decreases in the polymerized polyamide, which can result in a significant amount of phase separation exhibiting large polystyrene domains embedded in the polyamide.

[0020] The polyamide composition comprises an anionically polymerized polyamide and a thermoplastic polymer. The polyamide composition can comprise 5 to 50 weight percent (wt%), or 10 to 30 wt% of the thermoplastic polymer based on a total weight of the polyamide composition.

[0021] The anionically polymerized polyamide can have a weight average molecular weight of 2,000 to 100,000 Daltons (Da), or 5,000 to 50,000 Da as measured by gel permeation chromatography based on polystyrene standards.

[0022] The polyamide composition can have a crystallinity of 20 to 45 wt%, or 20 to 40 wt%, or 25 to 35 wt%, or 35 to 40 wt% as determined by differential scanning calorimetry (DSC). In determining the crystallinity using DSC, a polyamide composition having a size of 4.5 ± 0.1 milligram (mg) is sealed in a closed hermetic aluminum pan and heated at a heating rate of 10 degrees Celsius per minute ($^{\circ}\text{C}/\text{min}$) over a temperature range of -20 to 250 degrees Celsius ($^{\circ}\text{C}$). The weight percent crystallinity (X_c) is then determined by dividing the change in enthalpy of the polyamide composition measure from the DSC scan (ΔH_m) by the change in enthalpy of a 100 wt% crystalline sample of the same polyamide (ΔH_c) as shown in Equation (I).

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_c} \times 100 \quad (\text{I})$$

[0023] The polyamide composition can have a coefficient of linear thermal expansion (CLTE) as compared to a corresponding polyamide composition formed in the absence of a thermoplastic polymer. The polyamide composition can have a coefficient of linear thermal expansion of less than 110×10^{-5} inverse degrees Celsius ($^{\circ}\text{C}^{-1}$), or less than or equal to $108 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$, or 60×10^{-5} to $108 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$, or 60×10^{-5} to $105 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$. The coefficient of linear thermal expansion can be determined by forming a cylindrical sample having a 6 millimeter (mm) diameter and a 10 mm height and testing the samples in dynamic thermomechanical analysis (TMA) mode at a heating rate of $5 \text{ }^{\circ}\text{C}/\text{min}$ over the temperature range of 30 to $150 \text{ }^{\circ}\text{C}$. An average value of CLTE (α) over a temperature range of 30 to $150 \text{ }^{\circ}\text{C}$ is given using Equation (II)

$$\alpha = \frac{1}{l} \times \frac{l_2 - l_1}{T_2 - T_1} \quad (\text{II})$$

In Equation (II), l is the length at $30 \text{ }^{\circ}\text{C}$, l_1 is the length at T_1 ($30 \text{ }^{\circ}\text{C}$) and l_2 is the length at T_2 ($45 \text{ }^{\circ}\text{C}$).

[0024] A method of making the polyamide composition can comprise anionically polymerizing a monomer mixture comprising a cyclic lactam monomer, the thermoplastic polymer, a catalyst, and an activator to form the polyamide composition. The monomer mixture can further comprise a catalyst and an initiator. The polymerizing can comprise melt polymerizing at a temperature of greater than or equal to the melting temperature of the cyclic lactam monomer and below the melting point of the polymerizing polyamide. For

example, the melt polymerizing can occur at a temperature of 25 to 70 °C, or 80 to 220 °C, or 100 to 200 °C, or 145 to 165 °C. For cyclic lactam monomers containing less than 6 carbon atoms in the lactam ring, the melt polymerizing can occur at a temperature of less than or equal to 190 °C. When the cyclic lactam monomer comprises ϵ -caprolactam, then the melt polymerizing can occur at a temperature of 100 to 220 °C, or 145 to 165 °C.

[0025] The thermoplastic polymer can be soluble in the cyclic lactam monomer. For example, the thermoplastic polymer can be considered soluble in the cyclic lactam monomer if a monomer mixture comprising at least the cyclic lactam monomer and the thermoplastic polymer can comprise greater than 0 to 50 wt% of the dissolved thermoplastic polymer based on the total weight of the monomer mixture at 23 °C.

[0026] The thermoplastic polymer can comprise a polyether such as a poly(ether imide) (PEI), a poly(ether ketone) (PEK), a poly(ether ether ketone) (PEEK), a poly(ether ketone ketone) (PEKK), a poly(ether sulfone), a poly(ether ether sulfone) (PEES), or a combination comprising at least one of the foregoing. The thermoplastic polymer can comprise poly(ether imide), poly(ether ether sulfone), or a combination comprising at least one of the foregoing. The presence of one or both of poly(ether imide) and poly(ether ether sulfone) in the polyamide composition can beneficially result in one or both of a reduction in water absorption of the polyamide composition and an increase flame retardancy as compared to a corresponding polyamide composition formed in the absence of the thermoplastic polymer.

[0027] The thermoplastic polymer can comprise a copolymerizable repeat unit that is polymerizable with the cyclic lactam monomer. The thermoplastic polymer can comprise 0 to 5 mole percent (mol%) of a repeat unit that is polymerizable with the cyclic lactam monomer based on the total moles of repeat units of the thermoplastic polymer. The presence of a copolymerizable repeat unit can result in a cross-linking between the thermoplastic polymer and the polyamide.

[0028] The polyamide composition can further comprise an additional polymer. For example, the additional polymer can be present with the thermoplastic polymer during the polymerization of the cyclic lactam monomer. The additional polymer can be at least partially soluble in the cyclic lactam monomer. The additional polymer can comprise a polyacetal, a polyolefin, a polyacrylic, a polycarbonate, a polystyrene (PS), a polyester, a second polyamide, a polyamideimide, a polyarylate, a polyarylsulfone, a polyphenylene sulfide, a polyvinyl chloride, a polysulfone, a polyimide, a polyfluoroethylene, a

polybenzoxazole, a polyphthalide, a polyacetal, a polyanhydride, a polyvinyl ether, a polyvinyl thioether, a polyvinyl alcohol, a polyvinyl ketone, a polyvinyl halide, a polyvinyl nitrile, a polyvinyl ester, a polysulfonate, a polysulfide, a polythioester, a polysulfone, a polysulfonamide, a polyurea, a polyphosphazene, a polysilazane, polyphenylene oxide (PPO), or a combination comprising at least one of the foregoing. The polyamide composition can comprise a copolymerized siloxane that is polymerized simultaneously with the polyamide. For example, the copolymerized siloxane can be derived from octaphenylcyclotetrasiloxane.

[0029] The cyclic lactam monomer can comprise greater than or equal to 3 carbon atoms, or 3 to 14 carbon atoms, or 5 to 10 carbon atoms in the lactam ring. The cyclic lactam monomer can comprise β -propiolactam (also known as 2-azetidinone), γ -butyrolactam (also known as 2-pyrrolidone), δ -valerolactam (also known as 2-piperidine), ϵ -caprolactam, enantholactam, caprylolactam, lauro lactam, β,β -dimethylpropiolactam, α,α -dimethylpropiolactam, amyrolactam, or a combination comprising at least one of the foregoing. The cyclic lactam monomer can comprise an alkyl substituted cyclic lactam, an aryl substituted cyclic lactam, or a combination comprising at least one of the foregoing. The cyclic lactam monomer can comprise ϵ -caprolactam. The cyclic lactam monomer can comprise a combination comprising at least one of the foregoing cyclic lactam monomers.

[0030] The monomer mixture can comprise a catalyst. The catalyst can comprise an iminium salt that can be prepared by reacting a base with a lactam such as the cyclic lactam monomer. For example, the cyclic lactam monomer to be polymerized can be used for the preparation of the catalyst; but the catalyst can likewise be prepared from a different lactam. The iminium salt can be prepared by reacting the lactam with a metal compound. The metal compound can comprise a metal, a basic derivative of the metal, or a combination comprising at least one of the foregoing. The metal can comprise an alkali metal (such as sodium and potassium), an alkaline earth metal (such as magnesium), aluminum, or a combination comprising at least one of the foregoing. The basic derivative of the metal can comprise a hydroxide, an alkoxide, a hydride, an aryl, an amide, an organic acid salt, or a combination comprising at least one of the foregoing. The basic derivative of the metal can comprise sodium hydroxide, potassium hydroxide, lithium hydroxide, magnesium hydroxide, calcium hydroxide, strontium hydroxide, lithium hydride, sodium hydride, sodium methylate, sodium ethylate, sodium phenolate, sodium beta-naphtholate, sodamide, sodium stearate, lithium aluminium hydride, aluminium propylate, or a combination comprising at least one of the

foregoing. The catalyst can comprise sodium caprolactamate, such as C10 commercially available from BASF SE of Ludwigshafen, Germany.

[0031] The iminium salt can be prepared by adding the metal compound to the cyclic lactam monomer; or by first adding the metal compound to a portion of the cyclic lactam monomer and then adding the iminium salt to the remaining cyclic lactam monomer.

[0032] Little or no polymerization can occur during the preparation of the catalyst. The lactam can be as anhydrous as the metal compound. The catalyst can be present in an amount of 0.1 to 10 mol%, or 0.1 to 5 mol% based on the total moles of the lactam and catalyst. The catalyst can be present in an amount of 1 to 6 wt% based on a total weight of the monomer, activator, and catalyst. The more catalyst added, the lower the molecular weight of the resultant polyamide. The time used for the preparation of the catalyst depends upon the properties of the compounds employed, the quantity added, and the temperature chosen, and can generally be from a few seconds to several hours (hr). The iminium salt can be prepared by reacting the lactam with the metal compound by heating at a temperature of 25 to 220 °C.

[0033] The monomer mixture can comprise an activator (also referred to as a co-catalyst). The activator can comprise any compound that, in addition to the catalyst, brings about polymerization of the cyclic lactam monomer. The activator can comprise a carbodiimide (such as N,N'-diisopropyl carbodiimide, N,N'-di-(o-tolyl)-carbodiimide, N,N'-dicyclohexyl carbodiimide, 2,2',6,6'-tetraisopropyl diphenyl carbodiimide, or poly-(2,2-diisopropyl)-p-phenylene carbodiimide), a blocked or unblocked isocyanate (such as diphenyl methane diisocyanate, hexamethylene diisocyanate, toluol diisocyanate, isophorone diisocyanate, m-xylylene diisocyanate, p-xylylene diisocyanate, or phenyl isocyanate), an acylated lactam (such as an acetylated caprolactamate or laurin lactamate), oxazoline, a bisoxazoline (such as phenylene bisoxazoline), an oxazoline derivative, oxazolone, N-substituted 2-oxazolidone, a fatty alkyl oxazoline, a hydroxy-fatty alkyl oxazoline, an oxazoline produced with hydroxy acid (such as with ricinoleic acid), a lactam (such as bis-N-acyl lactam, N-acetyl caprolactam, N,N-terephthaloyl-bis-caprolactam, N,N'-sebacoyl-bis-caprolactam, and bifunctional hexamethylene-1,6-dicarbamoylcaprolactam), or a combination comprising at least one of the foregoing. The activator can comprise bifunctional hexamethylene-1,6-dicarbamoylcaprolactam, such as C20 commercially available from BASF SE of Ludwigshafen, Germany. The activator can comprise a multifunctional activator (such as poly(hexamethylene diisocyanate, poly[(phenyl

isocyanate)-co-formaldehyde], methyl isocyanate bound to polystyrene, 1-adamentyl isocyanate, or a combination comprising at least one of the foregoing. The activator can comprise a combination comprising at least one of the foregoing activators.

[0034] The activator can be present in an amount of 0.1 to 5 mol% based on the total moles of the cyclic lactam monomer. The activator can be present in an amount of 1 to 4 wt% based on a total weight of the monomer, activator, and catalyst. A molar ratio of the catalyst to the activator can be 0.5 to 2, or 0.8 to 1.2. The activator can be added before, during, or after adding the catalyst. The activator can be dissolved in a portion of the cyclic lactam monomer and the dissolved activator can be added as an activator mixture. Likewise, the catalyst can be dissolved in a portion of the cyclic lactam monomer and the dissolved catalyst can be added as a catalyst mixture.

[0035] The polymerization can be performed in an inert environment. For example, an inert gas (such as nitrogen, argon, and a noble gas) can be introduced onto the surface of the reaction mixture during the polymerization to prevent oxidation.

[0036] The polymerization can comprise polymerizing the reaction mixture in a batch reactor or in a mold. The polymerization can comprise mixing the thermoplastic polymer and the cyclic lactam monomer with one of the catalyst and the activator to form a monomer mixture, increasing the temperature of the monomer mixture to a polymerization temperature, and adding the other of the catalyst and the activator to initiate polymerization and form the polyamide composition.

[0037] The polymerizing can comprise reaction injection molding. Reaction injection molding can be useful in rapidly preparing cast articles of varying size and shape directly from the cyclic lactam monomer. In particular, reaction injection molding can have advantages when used in the manufacture of large molded articles, because reaction injection molding or similar processes use high temperatures and high pressures for their operations. Therefore, simpler and lighter weight molds can be employed and faster cycles can often be obtained in the manufacture of large shaped articles. The reaction injection molding can comprise injecting a single mixture comprising the cyclic lactam monomer, the thermoplastic polymer, the catalyst, and the activator into a mold; two or more mixtures can be mixed just prior to the injection molding; or the two or more mixtures can be simultaneously added to the mold during the injection molding. For example, a first mixture comprising the cyclic lactam monomer, the polymer, and one of the catalyst and the activator can be mixed with a

second mixture comprising the other of the catalyst and the activator just prior to the injection molding and the combined mixture can be injected into a mold to form the article.

[0038] The polymerizing can comprise resin transfer molding. In the resin transfer molding a preform can be positioned in a cavity of a molding tool, the molding tool can be closed and monomer mixture can be introduced into the cavity. The preform can comprise a resin transfer molding core with a fiber reinforcement material affixed to its outer surface. Internal communication passages can extend within an interior of the core, a first and a second internal communication passage each having an inlet opening and a discharge opening can extend through an outer surface of the core. The molding tool can have a first port and a second port. Fluid communication can be formed between the first port and the inlet opening of the first internal communication passage and between the second port and the discharge opening of the second internal communication passage. The monomer mixture can be introduced into the cavity through the first port, to and through the inlet opening of the first internal communication passage. The cavity can be vented through the discharge opening of the second internal communication passage, to and through the second port. The monomer mixture can then be cured to provide a fiber reinforced polyamide composition.

[0039] The polyamide composition can comprise an additive. The additive can comprise a filler (including glass fillers, ceramic or mineral fillers, or carbon fillers), an antioxidant, a blowing agent, a plasticizer, a colorant, or a combination comprising at least one of the foregoing. The additive can comprise eicosane, triacontane, a paraffin wax, or a combination comprising at least one of the foregoing. The additive can be present in an amount known in the art. For example, any additive (except filler) can be individually present in an amount of 0.01 to 5 wt%, based on the total weight of the polyamide composition. In general, the total amount of additives (except filler) does not total more than 10 wt% of the polyamide composition.

[0040] An article can comprise the polyamide composition. The article can be used in transportation vehicles (including cars, trucks, trains, planes, boats, jet skis, snow mobiles, motorcycles, helicopters, and the like).

[0041] The following examples are provided to illustrate the polyamide composition and the method of making the same. The examples are merely illustrative and are not intended to limit the polyamide composition made in accordance with the disclosure to the materials, conditions, or process parameters set forth therein.

Examples

[0042] In the examples, the following test methods were used.

[0043] Different scanning calorimetry was performed using a TA DSC Q200 to characterize the thermal transitions and crystallinity of polyamide compositions. The polyamide compositions had a size of 4.5 ± 0.1 mg and were tested at a heating rate of 10 °C/min over a temperature range of -20 to 250 °C. The samples were sealed in a closed hermetic aluminum pan prior to testing. The crystallinity of polyamide compositions was calculated using Equation (I). In Equation (I), ΔH_c for 100% crystalline polyamide 6 is 188 Joules per gram (J/g).

[0044] Thermogravimetric analysis (TGA) of the polyamide compositions was performed by increasing the temperature from 0 to 1,000 °C at a rate of 10 °C/min under a constant flow of nitrogen gas.

[0045] The coefficient of linear thermal expansion (CLTE) was measured by forming a cylindrical sample having 6 mm diameter and a 10 mm height and testing the samples in dynamic thermomechanical analysis (TMA) mode at a heating rate of 5 °C/min over the temperature range of 30 to 150 °C and evaluating using Equation (II).

Examples 1-12: Preparation of polyamide compositions

[0046] In Example 1, anionic polymerization of ϵ -caprolactam was carried out in a 20 milliliter (mL) glass vial under atmospheric pressure. The monomer mixture, comprising ϵ -caprolactam and the C20 activator, was melt mixed at a temperature of 150 °C under constant stirring. The polymerization was initiated upon addition of the C10 catalyst, where the monomer mixture comprised 94 wt% of the ϵ -caprolactam, 2 wt% of the C20 activator, 4 wt% of the C10 catalyst; all based on the total weight of the monomer mixture.

[0047] In Examples 2-12, anionic polymerization of ϵ -caprolactam was carried out in accordance with Example 1, except that an amount of a thermoplastic polymer was added to the monomer mixture and the C10 catalyst was added after the thermoplastic polymer fully dissolved in the monomer. In Examples 2-12, the same amounts of the ϵ -caprolactam, the C20 activator, and the C10 catalyst as used in Example 1 were used and an amount of the thermoplastic polymer was added such that the resultant monomer mixture comprised a wt% of the thermoplastic polymer based on the total weight of the monomer mixture as shown in Tables 1 and 2.

Table 1						
Example	1	2	3	4	5	6
Thermoplastic	-	PS	PS	PPO	PPO	PPO
Thermoplastic concentration (wt%)	-	10	100	10	20	100
Solubility Parameter ($J^{1/2}cm^{-3/2}$)	22.5	-	18.6	-	-	18.6
Crystallinity (wt%)	40.5	27.2	-	42.6	37.5	-

Example 13: Miscibility of the polyamide blends

[0048] SEM images of Examples 2, 4, 7, and 10 were taken and are shown in FIG. 1, FIG. 2, FIG. 3, and FIG. 4, respectively. FIG. 1 and FIG. 2 show that there is significant phase separation in the polyamide compositions comprising polystyrene and poly(phenylene oxide). Specifically, FIG. 1 shows that there are polystyrene domains on the order of tens of micrometers embedded in the polyamide and FIG. 2 shows the formation of two-phase domains as pointed out by the arrow comprising the phase separated poly(phenylene oxide) and the polyamide. Conversely, FIG. 3 and FIG. 4 show that there is little to no phase separation between the polyamide and poly(ether ether sulfone) and the poly(ether imide), respectively. Without being bound by theory, it is believed that the increased miscibility of the poly(ether ether sulfone) and the poly(ether imide) with the polyamide is due to the similar solubility parameters of the thermoplastic polymers and the polyamide. It is noted that for blends comprising poly(ether ether sulfone) and the poly(ether imide) at higher concentrations of 20 wt%, the formation of sub-micrometer domains can be observed in SEM images.

Table 2							
Example	1	7	8	9	10	11	12
Thermoplastic	-	PEES	PEES	PEES	PEI	PEI	PEI
Thermoplastic concentration (wt%)	-	5	10	100	10	20	100
Solubility Parameter ($J^{1/2}cm^{-3/2}$)	22.5	-	-	22.0	-	-	21.0
Crystallinity (wt%)	40.5	39.7	35.3	-	29.1	21.1	-
Density (g/cm^3)	1.14	1.15	1.13	1.37	1.12	1.10	1.27
Tg ($^{\circ}C$)	49.7	53.1	65.8	201.4	58.3	64.2	215.3

[0049] The DSC scans were also used to determine the crystallinity of the polyamide compositions and the results are shown in Tables 1 and 2. The crystallinity of the polyamide compositions comprising the poly(ether ether sulfone) and the poly(ether imide) exhibited a decrease in the crystallinity. This decrease is due to the increased weight fraction of the amorphous material in the compositions.

Example 14: Thermal stability of the polyamide compositions

[0050] Thermogravimetric analysis of the polyamide compositions of Examples 1 and 7-12 and the results are shown in FIG. 7 for compositions comprising poly(ether ether sulfone) and in FIG. 8 for compositions comprising poly(ether imide). FIG. 7 and FIG. 8 show that Examples 9 and 12 of the poly(ether ether sulfone) and the poly(ether imide) compositions, respectively both had an onset of degradation at 550 °C as compared to Example 1 comprising only the polyamide, which had an onset of degradation at only 300 °C. FIG. 7 and FIG. 8 show that the polyamide compositions comprising poly(ether ether sulfone) or the poly(ether imide) had both an increased onset and an increased offset of degradation as a function of their concentration in the polyamide composition, indicating an increased thermal stability as compared to Example 1.

Example 15: Coefficient of linear thermal expansion of the polyamide compositions

[0051] The CLTE of Examples 1, 8, and 10 were determined using thermomechanical analysis and the results are shown in Table 3 and in FIG 9. Table 3 shows that the CLTE of Examples 8 and 10 comprising the polyamide and a thermoplastic polymer is lower than the CLTE of Example 1 comprising only the polyamide. FIG. 9 shows the thermal expansion (change in length in micrometers divided by the initial length in millimeter) profile of Examples 1, 8, and 10 as the function of temperature. The thermal expansion of both Examples 8 and 10 are reduced as compared to Example 1. FIG. 9 further shows that the thermal expansion of Example 10 is less than that of Example 8. This further reduction in the thermal expansion of the composition comprising poly(ether imide) is in accordance with the higher T_g increase observed in DSC analysis.

Table 3			
Example	1	8	10
Thermoplastic	-	PEES	PEI
TP (wt%)	-	10	10
CLTE (10 ⁻⁵ °C ⁻¹)	110	104	80

[0052] Set forth below are non-limiting embodiments of the disclosure.

[0053] Embodiment 1: A polyamide composition, comprising: an anionically polymerized polyamide; and a thermoplastic polymer. A Hildebrand solubility factor of the anionically polymerized polyamide can be within 15% of a Hildebrand solubility factor of the thermoplastic polymer.

[0054] Embodiment 2: The polyamide composition of Embodiment 1, wherein the polyamide composition comprises 5 to 50 wt% of the thermoplastic polymer based on a total weight of the polyamide composition.

[0055] Embodiment 3: The polyamide composition of any one or more of the preceding embodiments, wherein the polyamide composition has a crystallinity of 20 to 45 wt% as determined using differential scanning calorimetry.

[0056] Embodiment 4: The polyamide composition of any one or more of the preceding embodiments, wherein the polyamide composition has a coefficient of linear thermal expansion that is less than a corresponding coefficient of linear thermal expansion of a comparison polyamide composition formed in the absence of the thermoplastic polymer.

[0057] Embodiment 5: The polyamide composition of any one or more of the preceding embodiments, wherein the polyamide composition has a coefficient of linear thermal expansion of less than $110 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$.

[0058] Embodiment 6: The polyamide composition of any one or more of the preceding embodiments, wherein the Hildebrand solubility factor of the anionically polymerized polyamide is within 10% of the Hildebrand solubility factor of the thermoplastic polymer.

[0059] Embodiment 7: The polyamide composition of any one or more of the preceding embodiments, wherein the Hildebrand solubility factor of the anionically polymerized polyamide is within 5% of the Hildebrand solubility factor of the thermoplastic polymer.

[0060] Embodiment 8: The polyamide composition of any one or more of the preceding embodiments, wherein the Hildebrand solubility factors of the thermoplastic polymer and of the anionically polymerized polyamide are each independently greater than or equal to $19 \text{ J}^{1/2}\text{cm}^{-3/2}$, or 19 to $25 \text{ J}^{1/2}\text{cm}^{-3/2}$.

[0061] Embodiment 9: The polyamide composition of any one or more of the preceding embodiments, wherein the Hildebrand solubility factors of the thermoplastic polymer and of the anionically polymerized polyamide are each independently greater than or equal to $20 \text{ J}^{1/2}\text{cm}^{-3/2}$, or 20 to $24 \text{ J}^{1/2}\text{cm}^{-3/2}$.

[0062] Embodiment 10: The polyamide composition of any one or more of the preceding embodiments, wherein the thermoplastic polymer comprises a poly(ether imide), a poly(ether ketone), a poly(ether ether ketone), a poly(ether ketone ketone), a poly(ether

sulfone), a poly(ether ether sulfone), or a combination comprising at least one of the foregoing.

[0063] Embodiment 11: The polyamide composition of any one or more of the preceding embodiments, wherein the thermoplastic polymer comprises a poly(ether imide), a poly(ether ether sulfone), or a combination comprising at least one of the foregoing.

[0064] Embodiment 12: The polyamide composition of any one or more of the preceding embodiments, wherein the anionically polymerized polyamide has a weight average molecular weight of 2,000 to 100,000 Daltons as measured by gel permeation chromatography based on polystyrene standards.

[0065] Embodiment 13: The polyamide composition of any one or more of the preceding embodiments, wherein the anionically polymerized polyamide is derived from a cyclic lactam monomer comprising β -propiolactam, γ -butyrolactam, δ -valerolactam, ϵ -caprolactam, enantholactam, caprylolactam, lauro lactam, β,β -dimethylpropiolactam, α,α -dimethylpropiolactam, amyrolactam, or a combination comprising at least one of the foregoing.

[0066] Embodiment 14: The polyamide composition of any one or more of the preceding embodiments, wherein the anionically polymerized polyamide is derived from a cyclic lactam monomer comprising ϵ -caprolactam.

[0067] Embodiment 15: The polyamide composition of any one or more of the preceding embodiments, wherein the polyamide composition further comprises an additional polymer different from the anionically polymerized polyamide and the thermoplastic polymer.

[0068] Embodiment 16: The polyamide composition of Embodiment 15, wherein the additional polymer comprises a polyacetal, a polyolefin, a polyacrylic, a polycarbonate, a polystyrene, a polyester, a second polyamide, a polyamideimide, a polyarylate, a polyarylsulfone, a polyphenylene sulfide, a polyvinyl chloride, a polysulfone, a polyimide, a polyfluoroethylene, a polybenzoxazole, a polyphthalide, a polyacetal, a polyanhydride, a polyvinyl ether, a polyvinyl thioether, a polyvinyl alcohol, a polyvinyl ketone, a polyvinyl halide, a polyvinyl nitrile, a polyvinyl ester, a polysulfonate, a polysulfide, a polythioester, a polysulfone, a polysulfonamide, a polyurea, a polyphosphazene, a polysilazane, a polyphenylene oxide, or a combination comprising at least one of the foregoing.

[0069] Embodiment 17: The polyamide composition of any one or more of the preceding embodiments, wherein the polyamide composition further comprises an additive.

[0070] Embodiment 18: A method of making any one or more of the preceding polyamide compositions, comprising: anionically polymerizing a monomer mixture comprising a cyclic lactam monomer, the thermoplastic polymer, a catalyst, and an activator to form the polyamide composition.

[0071] Embodiment 19: The method of Embodiment 18, wherein the cyclic lactam monomer comprises β -propiolactam, γ -butyrolactam, δ -valerolactam, ϵ -caprolactam, enantholactam, caprylolactam, laurolactam, β,β -dimethylpropiolactam, α,α -dimethylpropiolactam, amyrolactam, or a combination comprising at least one of the foregoing.

[0072] Embodiment 20: The method of Embodiment 19, wherein the cyclic lactam monomer comprises ϵ -caprolactam.

[0073] Embodiment 21: The method of any one or more of Embodiments 18 to 20, wherein the monomer mixture comprises 5 to 50 wt% of the thermoplastic polymer dissolved in the monomer mixture prior to the anionically polymerizing.

[0074] Embodiment 22: The method of any one or more of Embodiments 18 to 21, wherein the monomer mixture comprises 1 to 6 wt% of the catalyst based on the total weight of the monomer mixture.

[0075] Embodiment 23: The method of any one or more of Embodiments 18 to 22, wherein the monomer mixture comprises 1 to 4 wt% of the activator based on the total weight of the monomer mixture.

[0076] Embodiment 24: The method of any one or more of Embodiments 18 to 23, wherein the anionically polymerizing comprises reaction injection molding or resin transfer molding the monomer mixture.

[0077] Embodiment 25: An article comprising the polyamide composition of any one or more of the preceding embodiments.

[0078] Embodiment 26: The article of Embodiment 25, wherein the article is for use in a transportation vehicle.

[0079] While the disclosure has been described with reference to an exemplary embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the disclosure. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the disclosure without departing from the essential scope thereof. Therefore, it is intended that the disclosure not be limited to the particular

embodiment disclosed as the best mode contemplated for carrying out this disclosure, but that the disclosure will include all embodiments falling within the scope of the appended claims.

[0080] In general, the disclosure can alternately comprise, consist of, or consist essentially of, any appropriate components herein disclosed. The disclosure can additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any components, materials, ingredients, adjuvants or species used in the prior art compositions or that are otherwise not necessary to the achievement of the function and/or objectives of the present disclosure.

[0081] The terms “a” and “an” do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item. The term “or” means “and/or” unless clearly indicated otherwise by context. Reference throughout the specification to “an embodiment”, “another embodiment”, “some embodiments”, and so forth, means that a particular element (e.g., feature, structure, step, or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described elements may be combined in any suitable manner in the various embodiments. The terms “first,” “second,” and the like, as used herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. The term “combination” is inclusive of blends, mixtures, alloys, reaction products, and the like. Also, a list comprising “at least one or more of the foregoing” means that the list is inclusive of each element individually, as well as combinations of two or more elements of the list, and combinations of at least one element of the list with like elements not named.

[0082] In general, the compositions, methods, and articles can alternatively comprise, consist of, or consist essentially of, any ingredients, steps, or components herein disclosed. The compositions, methods, and articles can additionally, or alternatively, be formulated, conducted, or manufactured so as to be devoid, or substantially free, of any ingredients, steps, or components not necessary to the achievement of the function or objectives of the present claims. The notation “ $\pm 10\%$ ” means that the indicated measurement may be from an amount that is minus 10% to an amount that is plus 10% of the stated value.

[0083] Unless specified to the contrary herein, all test standards are the most recent standard in effect as of the filing date of this application, or, if priority is claimed, the filing date of the earliest priority application in which the test standard appears.

[0084] The endpoints of all ranges directed to the same component or property are inclusive of the endpoints, are independently combinable, and include all intermediate points and ranges. For example, ranges of “up to 25 wt%, or 5 to 20 wt%” is inclusive of the endpoints and all intermediate values of the ranges of “5 to 25 wt%,” such as 10 to 23 wt%, etc.

[0085] Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs.

[0086] All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference.

[0087] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

CLAIMS

What is claimed is:

1. A polyamide composition, comprising:
an anionically polymerized polyamide; and
a thermoplastic polymer;
wherein the Hildebrand solubility factor of the anionically polymerized polyamide is within 15% of the Hildebrand solubility factor of the thermoplastic polymer.
2. The polyamide composition of Claim 1, wherein the polyamide composition comprises 5 to 50 wt% of the thermoplastic polymer based on a total weight of the polyamide composition.
3. The polyamide composition of any one or more of the preceding claims, wherein the polyamide composition has a crystallinity of 20 to 45 wt% as determined using differential scanning calorimetry.
4. The polyamide composition of any one or more of the preceding claims, wherein the polyamide composition has a coefficient of linear thermal expansion that is less than a corresponding coefficient of linear thermal expansion of a comparison polyamide composition formed in the absence of the thermoplastic polymer.
5. The polyamide composition of any one or more of the preceding claims, wherein the polyamide composition has a coefficient of linear thermal expansion of less than $110 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$.
6. The polyamide composition of any one or more of the preceding claims, wherein the Hildebrand solubility factor of the anionically polymerized polyamide is within 5% of the Hildebrand solubility factor of the thermoplastic polymer.
7. The polyamide composition of any one or more of the preceding claims, wherein the thermoplastic polymer comprises a poly(ether imide), a poly(ether ketone), a poly(ether ether ketone), a poly(ether ketone ketone), a poly(ether sulfone), a poly(ether ether sulfone), or a combination comprising at least one of the foregoing.
8. The polyamide composition of any one or more of the preceding claims, wherein the thermoplastic polymer comprises a poly(ether imide), a poly(ether ether sulfone), or a combination comprising at least one of the foregoing.
9. The polyamide composition of any one or more of the preceding claims, wherein the anionically polymerized polyamide has a weight average molecular weight of

2,000 to 100,000 Daltons as measured by gel permeation chromatography based on polystyrene standards.

10. The polyamide composition of any one or more of the preceding claims, wherein the anionically polymerized polyamide is derived from a cyclic lactam monomer comprising β -propiolactam, γ -butyrolactam, δ -valerolactam, ϵ -caprolactam, enantholactam, caprylolactam, lauro lactam, β,β -dimethylpropiolactam, α,α -dimethylpropiolactam, amyrolactam, or a combination comprising at least one of the foregoing.

11. The polyamide composition of any one or more of the preceding claims, wherein the polyamide composition further comprises an additional polymer different from the anionically polymerized polyamide and the thermoplastic polymer.

12. The polyamide composition of Claim 11, wherein the additional polymer comprises a polyacetal, a polyolefin, a polyacrylic, a polycarbonate, a polystyrene, a polyester, a second polyamide, a polyamideimide, a polyarylate, a polyarylsulfone, a polyphenylene sulfide, a polyvinyl chloride, a polysulfone, a polyimide, a polyfluoroethylene, a polybenzoxazole, a polyphthalide, a polyacetal, a polyanhydride, a polyvinyl ether, a polyvinyl thioether, a polyvinyl alcohol, a polyvinyl ketone, a polyvinyl halide, a polyvinyl nitrile, a polyvinyl ester, a polysulfonate, a polysulfide, a polythioester, a polysulfone, a polysulfonamide, a polyurea, a polyphosphazene, a polysilazane, a polyphenylene oxide, or a combination comprising at least one of the foregoing.

13. The polyamide composition of any one or more of the preceding claims, wherein the polyamide composition further comprises an additive.

14. A method of making any one or more of the preceding polyamide compositions, comprising:

anionically polymerizing a monomer mixture comprising a cyclic lactam monomer, the thermoplastic polymer, a catalyst, and an activator to form the polyamide composition.

15. The method of Claim 14, wherein the cyclic lactam monomer comprises β -propiolactam, γ -butyrolactam, δ -valerolactam, ϵ -caprolactam, enantholactam, caprylolactam, lauro lactam, β,β -dimethylpropiolactam, α,α -dimethylpropiolactam, amyrolactam, or a combination comprising at least one of the foregoing.

16. The method of any one or more of Claims 14 to 15, wherein the monomer mixture comprises 5 to 50 wt% of the thermoplastic polymer dissolved in the monomer mixture prior to the anionically polymerizing.

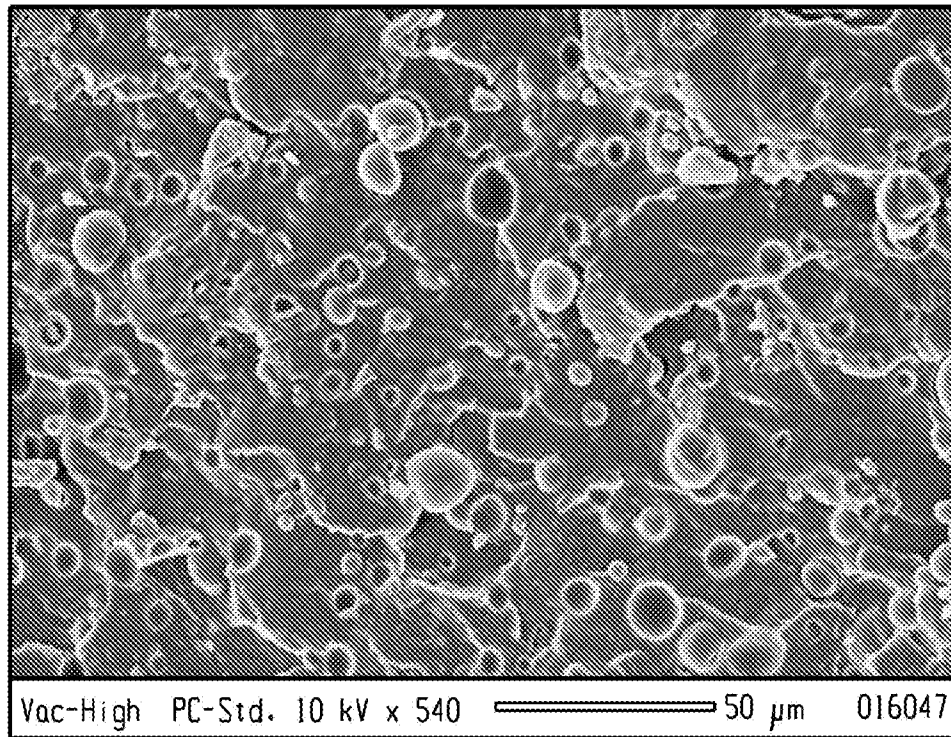
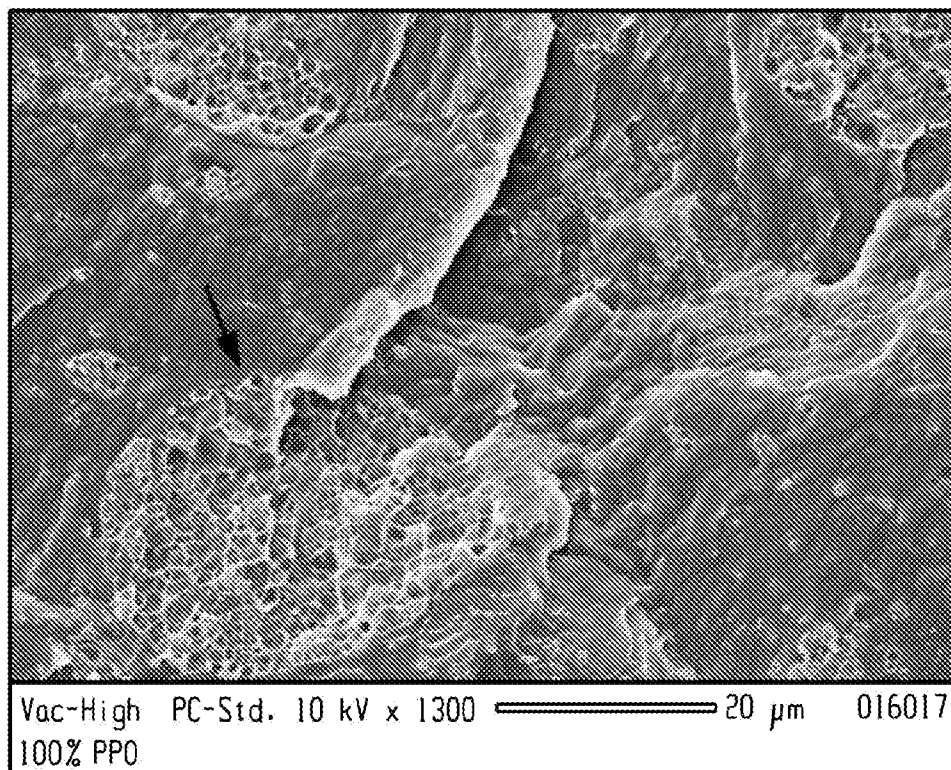
17. The method of any one or more of Claims 14 to 16, wherein the monomer mixture comprises 1 to 6 wt% of the catalyst based on the total weight of the monomer mixture.

18. The method of any one or more of Claims 14 to 17, wherein the monomer mixture comprises 1 to 4 wt% of the activator based on the total weight of the monomer mixture.

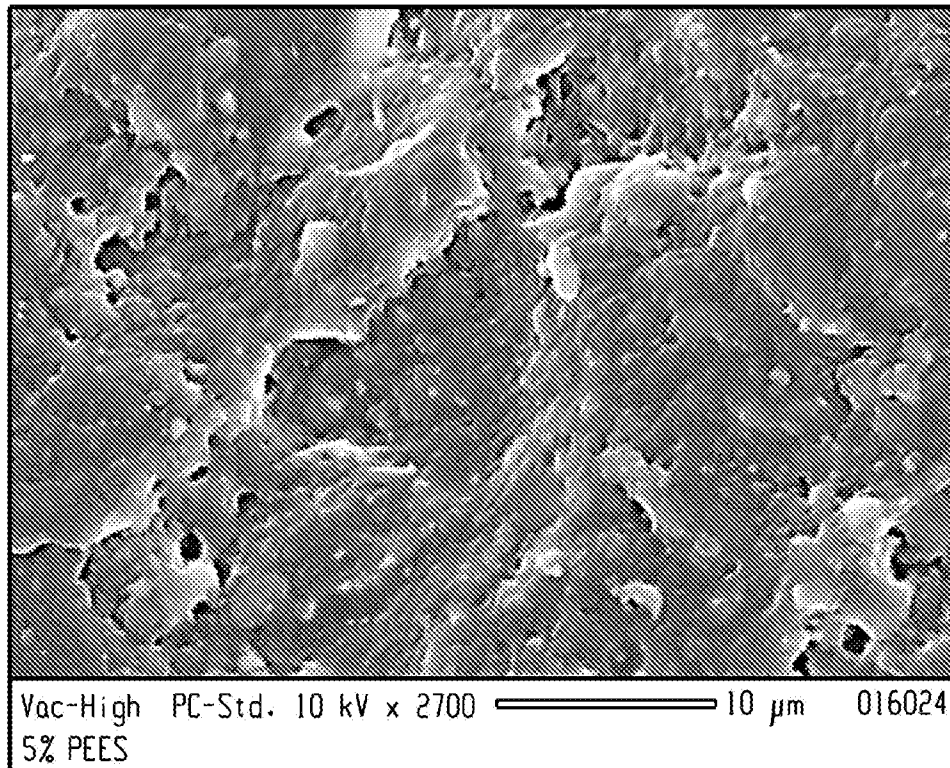
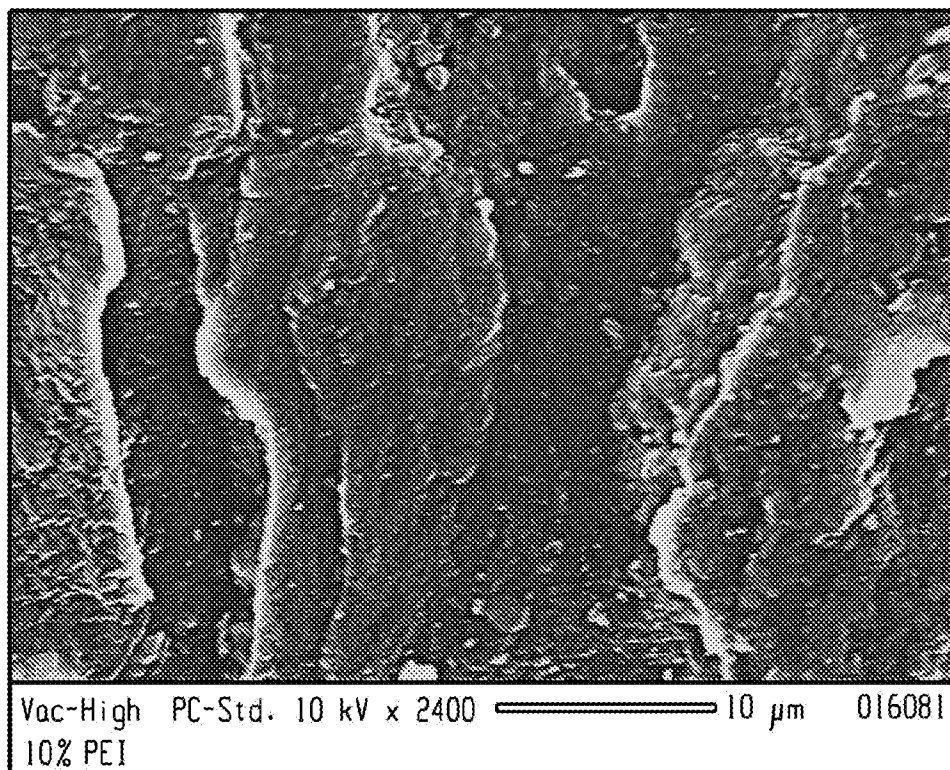
19. The method of any one or more of Claims 14 to 18, wherein the anionically polymerizing comprises reaction injection molding or resin transfer molding the monomer mixture.

20. An article comprising the polyamide composition of any one or more of the preceding claims.

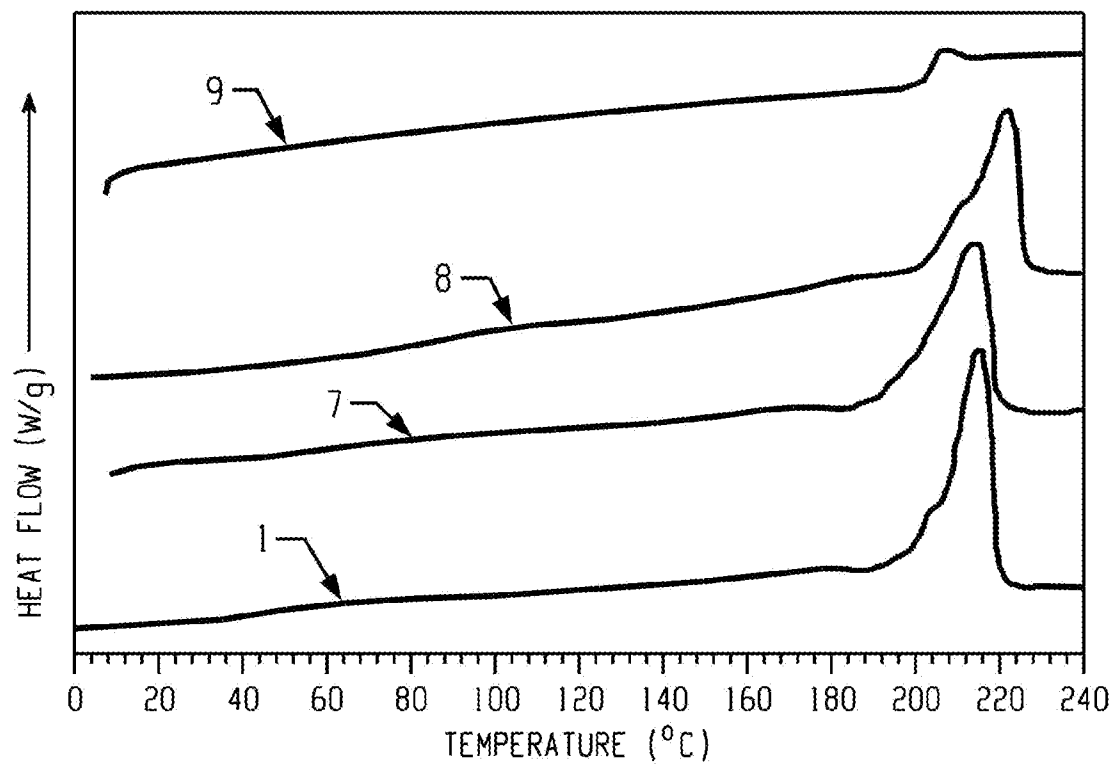
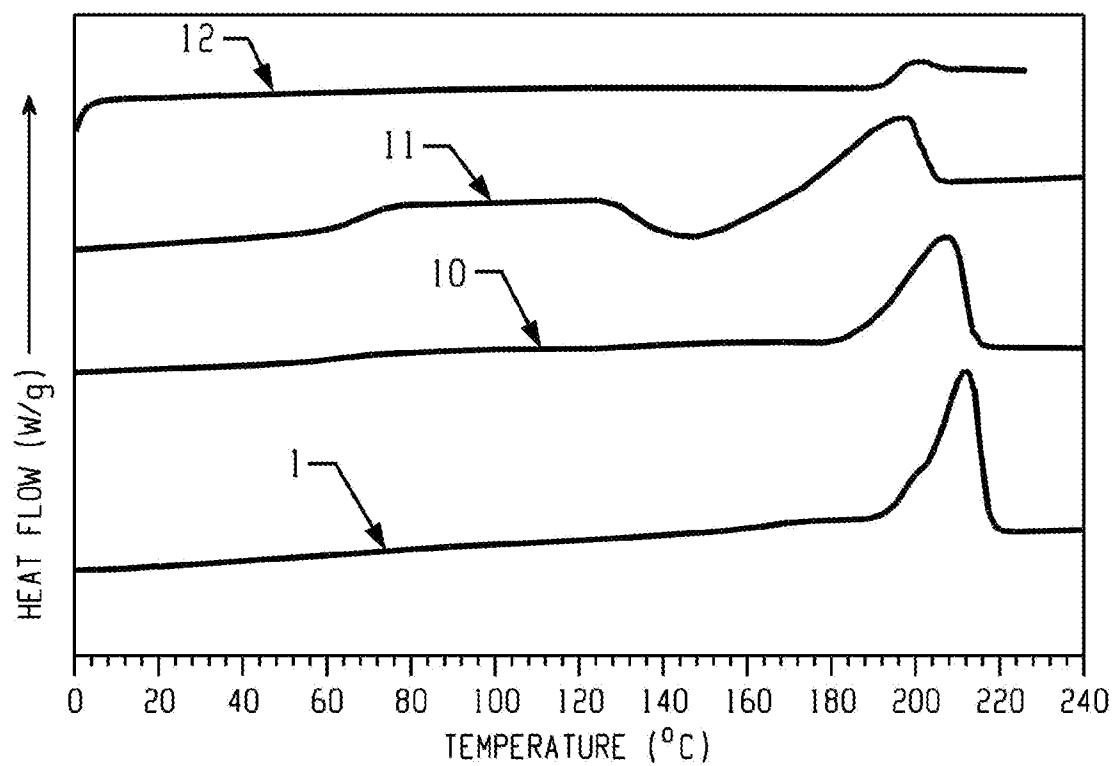
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*Fig. 1**Fig. 2*

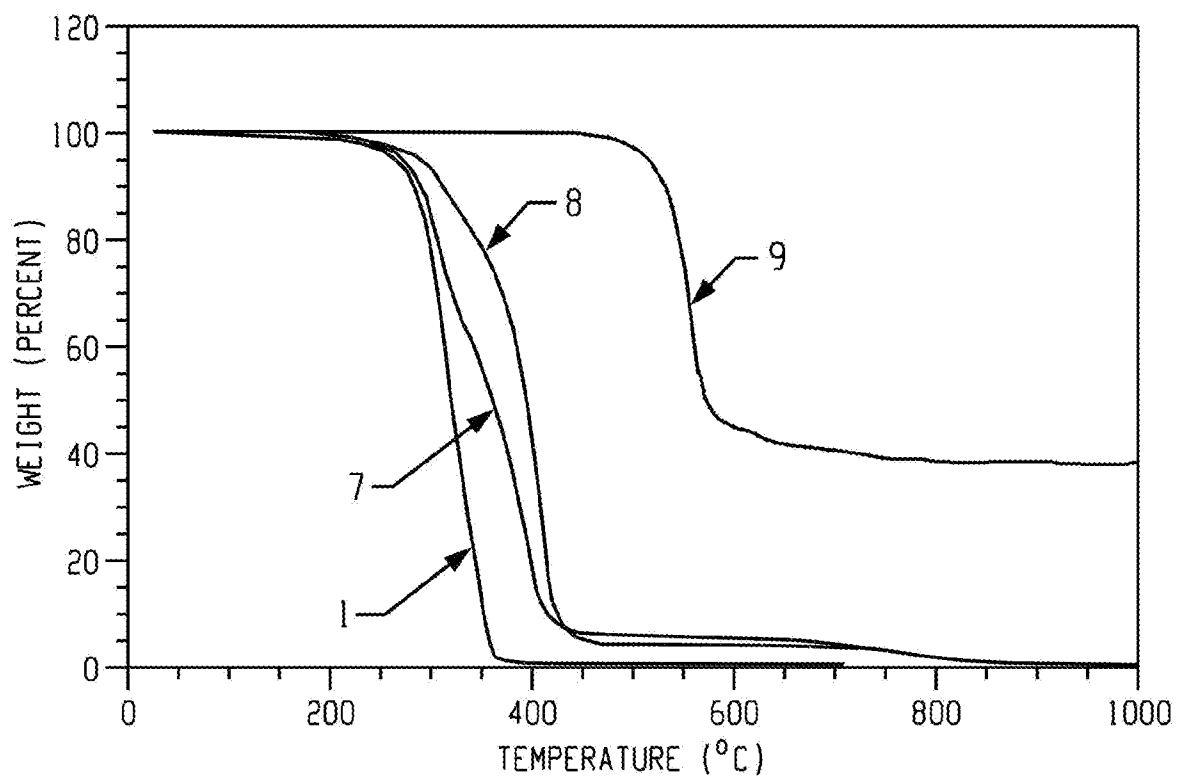
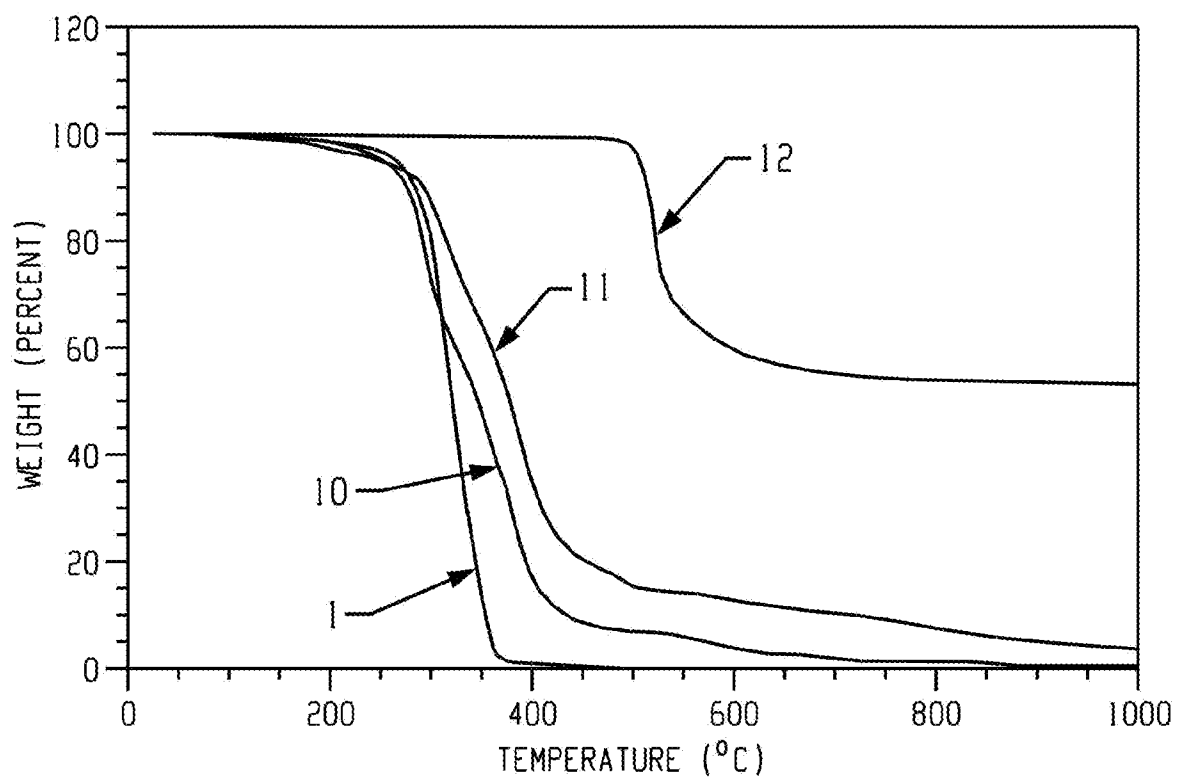
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*Fig. 3**Fig. 4*

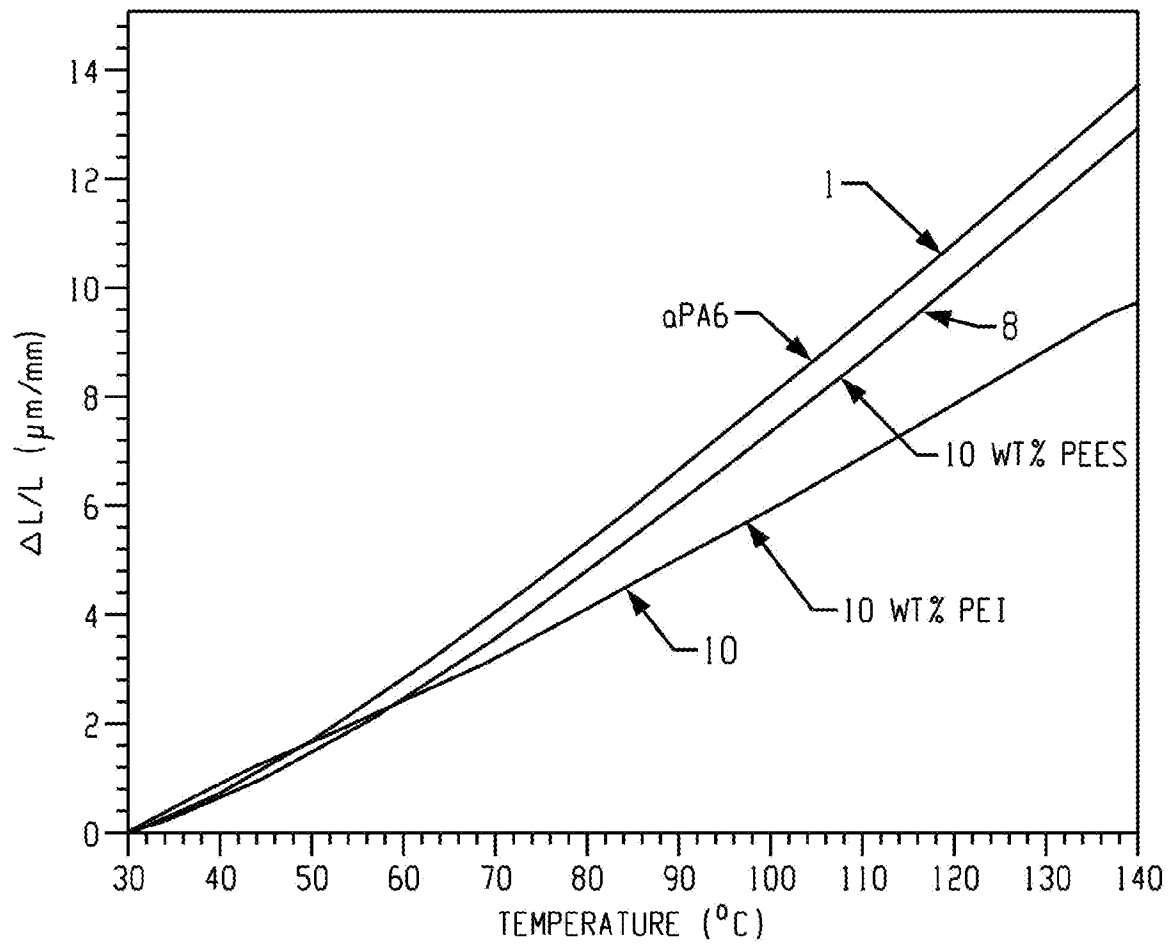
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*Fig. 5**Fig. 6*

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*Fig. 7**Fig. 8*

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*Fig. 9*

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US18/23273

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C08L 77/02, 83/04, 101/12 (2018.01)

CPC - C08L 77/02, 83/04, 101/12

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)

See Search History document

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

See Search History document

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2017/019979 A1 (UNIVERSITY OF MASSACHUSETTS, et al.) 02 February 2017; paragraphs [0019], [0022], [0026]-[0027], [0039], [0049]	1-2
Y	US 2012/0040185 A1 (TOPOLKARAEV, VA et al.) 16 February 2012; paragraphs [0002]-[0003], [0047]; claims 1-2	1-2
A	US 7,740,861 B2 (OSTROFF, GR) 22 June 2010; entire document	1-2

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

26 April 2018 (26.04.2018)

Date of mailing of the international search report

11 MAY 2018

Name and mailing address of the ISA/

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Authorized officer

Shane Thomas

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US18/23273

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 3-20
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.