**[07]** Therefore, there is a need for rapid processes and reagents that are useful for crystallizing PHA polymers. Such processes and reagents can be efficient, cost-saving, and suitable to large-scale processing of PHA materials.

**SUMMARY**

**[08]** The present disclosure provides a process for crystallizing a polymer having at least 20 mole percent of hydroxyalkanoate repeat units, comprising admixing the polymer and a compound with a crystal structure similar to the PHA crystal structure, such as pentaerythritol, providing heterogeneous nucleation sites.

**[09]** The present disclosure also provides a composition comprising a polymer having at least 20 mol percent of hydroxyalkanoate repeat units, and a compound that has allotropic character, such as sulfur and selenium.

**[09a]** In one aspect, the present disclosure provides a polymeric composition comprising:

a polymer including at least 20 mole percent hydroxyalkanoate repeat units, and

a nucleating agent, in an amount from 0.01% to 20% by weight of the polymer, wherein the nucleating agent is selected from the group consisting of (1) compounds having an orthorhombic crystal structure, (2) compounds having a hexagonal crystal structure, (3)allotropic elements having at least one crystalline form which is orthorhombic, hexagonal, or tetragonal, (4) polymorphic compounds having at least one crystalline form which is orthorhombic, or tetragonal, and (5) mixtures thereof;

wherein the polymer has a melting point from 100 °C to 150 °C.

**[09b]** In another aspect, the present disclosure provides a process for crystallizing a polymer, comprising the steps of:

admixing a polymer including at least 20 mole percent of hydroxyalkanoate repeat units with a nucleating agent, in an amount from 0.01% to 20% by weight of the polymer, at a first temperature, which is from 5°C to 15°C above the melting point of the polymer; and

cooling the mixture to a second temperature, which is from the glass transition temperature of the polymer to the melting point of the nucleating agent,

wherein the nucleating agent is selected from the group consisting of (1) compounds having an orthorhombic crystal structure, (2) compounds having a hexagonal crystal structure, (3) allotropic elements having at least one crystalline form which is orthorhombic, hexagonal, or tetragonal, (4) polymorphic compounds having at least one crystalline form which is orthorhombic, or tetragonal, and (5) mixtures thereof;

wherein the polymer has a melting point from 100 °C to 150 °C.

**[010]** The present disclosure also provides a polymeric composition which includes at least a polymer and a nucleating agent, in an amount from about 0.01% to about 20% by weight of the polymer. The polymer including at least 20 mole percent hydroxyalkanoate repeat units. The nucleating agent is selected from the group consisting of (1) compounds having an orthorhombic crystal structure, (2) compounds having a hexagonal crystal structure, (3) compounds having a tetragonal crystal structure, (4) allotrophic elements having at least one crystalline form which is orthorhombic, hexagonal, or tetragonal, (5) polymorphic compounds having at least one crystalline form which is orthorhombic, hexagonal, or tetragonal, and (6) mixtures thereof.

**[011]** The present disclosure further provides a process for crystallizing a polymer. According to one embodiment, the process includes a first step of admixing a

What is claimed is:

Claim 1. A polymeric composition comprising:

a polymer including at least 20 mole percent hydroxyalkanoate repeat units, and

a nucleating agent, in an amount from 0.01% to 20% by weight of the polymer, wherein the nucleating agent is selected from the group consisting of (1) compounds having an orthorhombic crystal structure, (2) compounds having a hexagonal crystal structure, (3) allotropic elements having at least one crystalline form which is orthorhombic, hexagonal, or tetragonal, (4) polymorphic compounds having at least one crystalline form which is orthorhombic, or tetragonal, and (5) mixtures thereof;

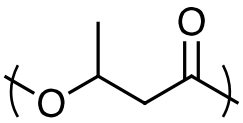
wherein the polymer has a melting point from 100 °C to 150 °C.

Claim 2. The polymeric composition of Claim 1, wherein the nucleating agent is selected from the group consisting of dipentaerythritol, anatase, wulfenite, aragonite, sulfur, selenium, phosphorous, benzamide, and mixtures thereof.

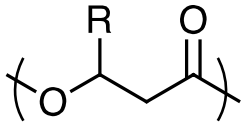
Claim 3. The polymeric composition of Claim 1, wherein the nucleating agent is present in an amount from 0.5% to 5% by weight of the polymer.

Claim 4. The polymeric composition of Claim 1, wherein the polymer is hydroxybutyrate-hydroxyhexanoate copolymer.

Claim 5. The polymeric composition of Claim 1, wherein the polymer has a first repeat unit having the structure:



and a second repeat unit having the structure:




wherein each R is independently a $C_3$ to $C_{19}$ alkyl group, and

wherein the polymer includes from 75 mole percent to 99 mole percent of the first repeat unit and from 1 mole percent to 25 mole percent of the second repeat unit.

Claim 6. The polymeric composition of Claim 1, wherein the polymer has a weight average molecular weight from 10,000 to 3,000,000 daltons.

Claim 7. The polymeric composition of Claim 1, wherein the polymer has a glass transition temperature from -30 °C to 10 °C.

Claim 8. A process for crystallizing a polymer, comprising the steps of:

admixing a polymer including at least 20 mole percent of hydroxyalkanoate repeat units with a nucleating agent, in an amount from 0.01% to 20% by weight of the polymer, at a first temperature, which is from 5°C to 15°C above the melting point of the polymer; and

cooling the mixture to a second temperature, which is from the glass transition temperature of the polymer to the melting point of the nucleating agent,

wherein the nucleating agent is selected from the group consisting of (1) compounds having an orthorhombic crystal structure, (2) compounds having a hexagonal crystal structure, (3) allotropic

elements having at least one crystalline form which is orthorhombic, hexagonal, or tetragonal, (4) polymorphic compounds having at least one crystalline form which is orthorhombic, or tetragonal, and (5) mixtures thereof;

wherein the polymer has a melting point from 100 °C to 150 °C.

Claim 9. The method of Claim 8, wherein the first temperature is from 100 °C to 190 °C.

Claim 10. The method of Claim 8, wherein the second temperature is from 50 °C to 90 °C.

Claim 11. The method of Claim 8, wherein the nucleating agent is selected from the group consisting of dipentaerythritol, anatase, wulfenite, aragonite, sulfur, selenium, phosphorous, benzamide, and mixtures thereof.

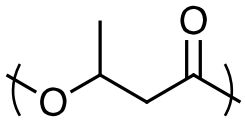
Claim 12. The method of Claim 8, wherein the nucleating agent is present in an amount from 0.5% to 5% by weight of the polymer.

Claim 13. The method of Claim 8, wherein the polymer is hydroxybutyrate-hydroxyhexanoate copolymer.

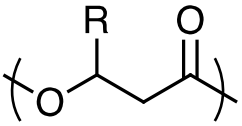
Claim 14. The method of Claim 8, wherein the polymer has a weight average molecular weight from 10,000 to 3,000,000 daltons.

Claim 15. The method of Claim 8, wherein the polymer has a glass transition temperature from -30 °C to 10 °C.

Claim 16. The method of Claim 8, wherein the polymer has a first repeat unit having the structure:



and a second repeat unit having the structure:



wherein each R is independently a $C_3$ to $C_{19}$ alkyl group, and

wherein the polymer includes from 75 mole percent to 99 mole percent of the first repeat unit and from 1 mole percent to 25 mole percent of the second repeat unit.