CLAIMS

Claim 1. A method for mitigating polymer degradation in poly(hydroxyalkanoates), the method comprising:

combining at least one poly(hydroxyalkanoate) with an end-capping agent, at least one acid anhydride, and a peroxide to form a reaction mixture comprising at least 50 weight percent of the at least one poly(hydroxyalkanoate), from 0.01 to 15 weight percent of the end-capping agent, from 0.01 to 15 weight percent of the acid anhydride, and from 0.01 to 0.5 weight percent of the peroxide, wherein the at least one poly(hydroxyalkanoate) comprises carboxylic acid end groups and monomeric repeat units which are susceptible to degradation to form unsaturated carboxylic acid by-products;

reacting the end-capping agent with the carboxylic acid end groups to form end-capping groups on the at least one poly(hydroxyalkanoate); and

reacting the at least one acid anhydride and the peroxide with the at least one poly(hydroxyalkanoate) to graft side chains formed from the acid anhydride onto the at least one poly(hydroxyalkanoate),

wherein the end-capping agent comprises at least one compound selected from the group consisting of carbodiimides, diisocyanates, epoxides, and mixtures thereof, and

wherein the at least one acid anhydride comprises a cyclic or noncyclic acid anhydride having from 3 to 40 carbon atoms.

Claim 2. The method of Claim 1, wherein the at least one poly(hydroxyalkanoate) has an initial weight average molecular weight before combining with the end-capping agent and the acid anhydride, of at least 10,000 Daltons, as determined by ASTM 5296-19.

Claim 3. The method of Claim 1 or Claim 2, wherein the at least one poly(hydroxyalkanoate) has an initial weight average molecular weight before combining with an end-capping agent and the acid anhydride, from 20,000 Daltons to 2,500,000 Daltons, as determined by ASTM 5296-19.

Claim 4. The method of any one of Claims 1 to 3, wherein the at least one poly(hydroxyalkanoate) comprises 3-hydroxybutyrate monomeric repeat units, which are susceptible to degradation to form crotonic acid.

Claim 5. The method of any one of Claims 1 to 3, wherein the at least one poly(hydroxyalkanoate) comprises 3-hydroxyhexanoate monomeric repeat units, which are susceptible to degradation to form hexenoic acid.

Claim 6. The method of any one of Claims 1 to 3, wherein the at least one poly(hydroxyalkanoate) comprises 3-hydroxypropionate monomeric repeat units, which are susceptible to degradation to form acrylic acid.

Claim 7. The method of any one of Claims 1 to 3, wherein the at least one poly(hydroxyalkanoate) comprises 4-hydroxybutyrate monomeric repeat units, which are susceptible to degradation to form 4-hydroxybutyric acid.

Claim 8. The method of any one of Claims 1 to 3, wherein the at least one poly(hydroxyalkanoate) comprises poly-3-hydroxybutyrate-co-3-hydroxyhexanoate (P3HB-co-P3HHx).

Claim 9. The method of any one of Claims 1 to 3, wherein the at least one poly(hydroxyalkanoate) comprises polyhydroxybutyrate homopolymer.

Claim 10. The method of any one Claims 1 to 3, wherein the at least one poly(hydroxyalkanoate) comprises poly-3-hydroxybutyrate-co-3-hydroxyvalerate.

Claim 11. The method of any one of Claims 1 to 3, wherein the at least one poly(hydroxyalkanoate) comprises from 0.1 to 25 mole percent monomer residues of a 3-hydroxyalkanoate selected from the group consisting of 3-hydroxyhexanoate, 3-hydroxyoctanoate, 3-hydroxydecanoate, and mixtures thereof.

Claim 12. The method of any one of Claims 1 to 3, wherein the at least one poly(hydroxyalkanoate) comprises a polyhydroxyalkanoate terpolymer made up from 75 to 99.9 mole percent monomer residues of 3-hydroxybutyrate, from 0.1 to 25 mole percent monomer residues of 3-hydroxyhexanoate, and from 0.1 to 25 mole percent monomer residues of a third 3-hydroxyalkanoate selected from the group consisting of 3-hydroxyoctanoate, 3-hydroxydecanoate, and mixtures thereof.

Claim 13. The method of any one of Claims 1 to 3, wherein the end-capping agent comprises at least one carbodiimide according to Formula (I)

$$R^1 – N = C = N – R^2$$

Formula (I)

wherein R^1 and R^2 independently comprise an aliphatic or aromatic group, optionally substituted with one or more heteroatoms selected from the group consisting of N, O, S, and P.

Claim 14. The method of any one of Claims 1 to 13, wherein the end-capping agent comprises at least one polymeric carbodiimide having a molecular weight from 20 to 5000 Daltons, as determined by ASTM 5296-19.

Claim 15. The method of any one of Claims 1 to 13, wherein the end-capping agent comprises at least one diisocyanate according to Formula (II)

$O = C = N - R^3 – N = C = O$

Formula (II)

wherein R^3 comprises an aliphatic or aromatic group having from 1 to 20 carbon atoms.

Claim 16. The method of any one of Claims 1 to 13, wherein the end-capping agent comprises at least one aliphatic or aromatic epoxide having from 2 to 200 carbon atoms.

Claim 17. The method of any one of Claims 1 to 13, wherein the end-capping agent comprises at least one poly(epoxide) having a molecular weight from 40 to 5000 Daltons, as determined by ASTM 5296-19.

Claim 18. The method of any one of Claims 1 to 17, wherein the at least one acid anhydride is an aliphatic cyclic acid anhydride having from 3 to 40 carbon atoms.

Claim 19. The method of any one of Claims 1 to 17, wherein the at least one acid anhydride comprises at least one cyclic anhydride selected from the group consisting of maleic anhydride, succinic anhydride, octadecenyl succinic anhydride, and mixtures thereof.

Claim 20. The method of any one of Claims 1 to 19, wherein the reacting step is carried out at a temperature from 120 °C to 200 °C.

Claim 21. The method of any one of Claims 1 to 20, wherein the peroxide is an organic peroxide.

Claim 22. The method of any one of Claims 1 to 21, wherein the peroxide is selected from the group consisting of lauryl peroxide, dicumyl peroxide, and 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane

Claim 23. The method of any one of Claims 1 to 22, wherein the reacting step is carried out in an extruder.

Claim 24. The method of any one of Claims 1 to 22, wherein the reacting step is carried out in a continuous mixer.

Claim 25. A polymer composition comprising at least 50 weight percent of the end-capped and grafted poly(hydroxyalkanoate) formed according to the method of any one of Claims 1 to 24.