Claims (Article 34)

1. A biodegradable film, which is prepared from a composition comprising: a copolyester obtained by extrusion reaction of a branched aliphatic-aromatic copolyester derived from monomer a, monomer b, monomer c and monomer d with an organic peroxide, wherein the monomer a is an aromatic dibasic acid or an ester derivative thereof; the monomer b is one or more of C_2-C_{10} aliphatic dihydric alcohols or C_3-C_{10} alicyclic dihydric alcohols; the monomer c is a C_4-C_{20} aliphatic dibasic acid or an ester derivative thereof; the monomer d is one or more of polyols with a functionality of more than 2, polycarboxylic acids with a functionality of more than 2, anhydrides with a functionality of more than 2, epoxy compounds or anhydrides with hydroxyl or carboxyl group, glycidyl ester, glycidyl ether, glycidol, lactones or cyclic carbonates with hydroxyl or carboxyl side group; the branched aliphatic-aromatic copolyester is obtained by reacting monomer a, monomer b, monomer c and monomer d under the action of a catalyst system containing a second catalyst, wherein the second catalyst is a compound of $RE(R^3)_3$, wherein RE is a rare earth metal element, R^3 is at least one selected from the group consisting of halogen, alkoxy group, aryloxy group, acetylacetone group and R^4COO- group, wherein R^4 is C_1-C_{30} alkyl group.

~~2. The biodegradable film as claimed in claim 1, wherein the branched aliphatic-aromatic copolyester is obtained by reacting monomer a, monomer b, monomer c and monomer d under the action of a catalyst system containing a second catalyst, wherein the second catalyst is a compound of $RE(R^3)_3$, wherein RE is a rare earth metal element, R^3 is at least one selected from the group consisting of halogen, alkoxy group, aryloxy group, acetylacetone group and R^4COO- group, wherein R^4 is C_1-C_{30} alkyl group.~~

~~3~~2. The biodegradable film as claimed in claim ~~2~~1, wherein, in the

compound of $RE(R^3)_3$ as the second catalyst, RE is lanthanum, cerium, praseodymium, neodymium, terbium, ytterbium, dysprosium, samarium or scandium; the halogen is chlorine or bromine, the alkoxy group is C_3-C_6 alkoxy group, the aryloxy group is aryloxy group comprising at least one benzene ring and/or naphthalene ring, and R^4 is C_1-C_{20} alkyl group.

43. The biodegradable film as claimed in claim ~~2~~1, wherein the catalyst system further comprises a first catalyst and/or a third catalyst; wherein the first catalyst is one or more selected from the group consisting of an oxide of M, $M(OR^1)_n$ and $M(OOCR^2)_m$, wherein M is titanium, antimony or zinc, n and m are each independently the valence of M, R^1 is C_1-C_{10} alkyl group, and R^2 is C_1-C_{20} alkyl group; the third catalyst is at least one organotin compound.

~~5~~4. The biodegradable film as claimed in claim 43, wherein the molar ratio of the catalyst in its entirety to the monomer (a + c) is 1: 1000-20000, and the molar ratio of the first catalyst to the second catalyst to the third catalyst is 0-20: 0.1-10: 0-1, preferably 0.1-20: 0.1-10: 1.

~~6~~5. The biodegradable film as claimed in any one of claims 1-~~5~~4, wherein the amounts of various monomers are as follows: the molar ratio of (a + c) to b is 1: 0.8-3, the molar ratio of (a + c) to d is 100-2000: 1, the molar ratio of a to c is 0: 100-95: 5, preferably 0: 100-60: 40.

~~7~~6. The biodegradable film as claimed in any one of claims 1-~~6~~5, wherein the monomer a is selected from terephthalic acid or dimethyl terephthalate; the monomer b is selected from ethylene glycol, 1,3-propanediol or 1,4-butanediol; the monomer c is selected from succinic acid, succinic anhydride, dimethyl succinate, adipic acid or dimethyl adipate; the monomer d is selected from pyromellitic dianhydride, glycerol, pentaerythritol, glycidyl succinate, glycidyl

adipate, glycidyl terephthalate, ethylene glycol glycidyl ether, 1,4-butanediol glycidyl ether, glycidic acid, glycidol, 3-hydroxyphthalic anhydride, 4-hydroxyphthalic anhydride, 3-hydroxymethylcaprolactone, a five-membered or six-membered cyclic carbonate with an alkylhydroxy group or an alkylcarboxyl group.

~~8~~7. The biodegradable film as claimed in any one of claims 1-~~7~~6, wherein the branched aliphatic-aromatic copolyester is prepared as follows: under the action of a catalyst system, monomer a, monomer b, monomer c and monomer d are mixed for esterification or transesterification reaction, or the esterification or transesterification product of monomer a and monomer b and the esterification or transesterification product of monomer c and monomer d are mixed for copolycondensation reaction.

~~9~~8. The biodegradable film as claimed in any one of claims 1-~~8~~7, wherein the branched aliphatic-aromatic copolyester has a melt index of 2-100g/10min, preferably 5-100g/10min at 190℃ under a load of 2.16 kg.

~~10~~9. The biodegradable film as claimed in any one of claims 1-~~9~~8, wherein the organic peroxide is selected from dialkyl peroxides, diacyl peroxides or peroxyesters.

~~11~~10. The biodegradable film as claimed in claim ~~10~~9, wherein the dialkyl peroxide is selected from dicumyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane or di(tert-butylperoxyisopropyl)benzene; the diacyl peroxide is selected from benzoyl peroxide or lauroyl peroxide.

~~12~~11. The biodegradable film as claimed in any one of claims 1-~~11~~10,

wherein the organic peroxide is used in an amount of 0.01 to 5wt% based on the amount of the branched aliphatic-aromatic copolyester.

~~13~~12. The biodegradable film as claimed in any one of claims 1-~~12~~11, wherein the copolyester has a melt index of 0.1 to 10g/10min at 190℃ under a load of 2.16 kg.

~~14~~13. The biodegradable film as claimed in any one of claims 1-~~13~~12, wherein the composition also comprises additives, and the additives include an antioxidant, a slipping agent, an anti-blocking agent and a nucleating agent.

~~15~~14. The biodegradable film as claimed in claim ~~14~~13, wherein the amount of the antioxidant is 0.05-5 parts, the amount of the slipping agent is 0.05-5 parts, the amount of the anti-blocking agent is 0.05-5 parts, and the amount of the nucleating agent is 0.1-20 parts based on 100 parts by weight of the copolyester.

~~16~~15. The biodegradable film as claimed in any one of claims ~~14-15~~13-14, wherein the antioxidant is a mixture of a hindered phenol antioxidant and a phosphite antioxidant in a mass ratio of 1: 1.

~~17~~16. The biodegradable film as claimed in claim ~~16~~15, wherein the hindered phenol antioxidant is selected from antioxidant 1010, antioxidant 1076, antioxidant 245 or antioxidant 246; the phosphite antioxidant is selected from triphenyl phosphate, trimethyl phosphate or antioxidant 168.

~~18~~17. The biodegradable film as claimed in any one of claims ~~14-15~~13-14, wherein the slipping agent is stearate or organic carboxylic acid amide, wherein the stearate is preferably calcium stearate, and the organic carboxylic acid amide

is preferably erucamide or oleamide;

the anti-blocking agent is silica or talc;

the nucleating agent is selected from hyperbranched polyamides, low density polyethylene or ethylene-methacrylic acid ionomers.

~~19~~18. A method for preparing the biodegradable film as claimed in any one of claims 1-~~18~~17, the method comprising the steps of:

1) preparing a copolyester by extrusion reaction of a branched aliphatic-aromatic copolyester derived from monomer a, monomer b, monomer c and monomer d with an organic peroxide;

the monomer a is an aromatic dibasic acid or an ester derivative thereof; the monomer b is one or more of C_2-C_{10} aliphatic dihydric alcohols or C_3-C_{10} alicyclic dihydric alcohols; the monomer c is a C_4-C_{20} aliphatic dibasic acid or an ester derivative thereof; the monomer d is one or more of polyols with a functionality of more than 2, polycarboxylic acids with a functionality of more than 2, anhydrides with a functionality of more than 2, epoxy compounds or anhydrides with hydroxyl or carboxyl group, glycidyl ester, glycidyl ether, glycidol, lactones or cyclic carbonates with hydroxyl or carboxyl side group;

the branched aliphatic-aromatic copolyester is obtained by reacting monomer a, monomer b, monomer c and monomer d under the action of a catalyst system containing a second catalyst, wherein the second catalyst is a compound of $RE(R^3)_3$, wherein RE is a rare earth metal element, R^3 is at least one selected from the group consisting of halogen, alkoxy group, aryloxy group, acetylacetone group and R^4COO- group, wherein R^4 is C_1-C_{30} alkyl group;

2) extruding and granulating the copolyester obtained in the step 1) to obtain a composition; and

3) blowing the composition to obtain the biodegradable film.

~~20. The method as claimed in claim 19, wherein the branched~~

~~aliphatic-aromatic copolyester is obtained by reacting monomer a, monomer b, monomer c and monomer d under the action of a catalyst system containing a second catalyst, wherein the second catalyst is a compound of $RE(R^3)_3$, wherein RE is a rare earth metal element, R^3 is at least one selected from the group consisting of halogen, alkoxy group, aryloxy group, acetylacetone group and R^4COO- group, wherein R^4 is C_1-C_{30} alkyl group.~~

~~21~~19. The method as claimed in claim ~~20~~18, wherein, in the compound of $RE(R^3)_3$ as the second catalyst, RE is lanthanum, cerium, praseodymium, neodymium, terbium, ytterbium, dysprosium, samarium or scandium; the halogen is chlorine or bromine, the alkoxy group is C_3-C_6 alkoxy group, the aryloxy group is aryloxy group comprising at least one benzene ring and/or naphthalene ring, and R^4 is C_1-C_{20} alkyl group.

~~22~~20. The method as claimed in claim ~~20~~18, wherein the catalyst system further comprises a first catalyst and/or a third catalyst; wherein the first catalyst is one or more selected from the group consisting of an oxide of M, $M(OR^1)_n$ and $M(OOCR^2)_m$, wherein M is titanium, antimony or zinc, n and m are each independently the valence of M, R^1 is C_1-C_{10} alkyl group, and R^2 is C_1-C_{20} alkyl group; the third catalyst is at least one organotin compound.

~~23~~21. The method as claimed in claim ~~22~~20, wherein the molar ratio of the catalyst in its entirety to the monomer (a + c) is 1: 1000-20000, and the molar ratio of the first catalyst to the second catalyst to the third catalyst is 0-20: 0.1-10: 0-1, preferably 0.1-20: 0.1-10: 1.

~~24~~22. The method as claimed in any one of claims ~~19-23~~18-21, wherein the amounts of various monomers are as follows: the molar ratio of (a + c) to b is 1: 0.8-3, the molar ratio of (a + c) to d is 100-2000: 1, the molar ratio of a to c is 0:

100-95: 5, preferably 0: 100-60: 40.

~~25~~23. The method as claimed in any one of claims ~~19-24~~18-22, wherein the monomer a is selected from terephthalic acid or dimethyl terephthalate; the monomer b is selected from 1,3-propanediol or 1,4-butanediol; the monomer c is selected from succinic acid, succinic anhydride, dimethyl succinate, adipic acid or dimethyl adipate; the monomer d is selected from pyromellitic dianhydride, glycerol, pentaerythritol, glycidyl succinate, glycidyl adipate, glycidyl terephthalate, ethylene glycol glycidyl ether, 1,4-butanediol glycidyl ether, glycidic acid, glycidol, 3-hydroxyphthalic anhydride, 4-hydroxyphthalic anhydride, 3-hydroxymethylcaprolactone, a five-membered or six-membered cyclic carbonate with an alkylhydroxy group or an alkylcarboxyl group.

~~26~~24. The method as claimed in any one of claims ~~19-25~~18-23, wherein the branched aliphatic-aromatic copolyester is prepared as follows: under the action of a catalyst system, monomer a, monomer b, monomer c and monomer d are mixed for esterification or transesterification reaction, or the esterification or transesterification product of monomer a and monomer b and the esterification or transesterification product of monomer c and monomer d are mixed for copolycondensation reaction.

~~27~~25. The method as claimed in any one of claims ~~19-26~~18-24, wherein the branched aliphatic-aromatic copolyester has a melt index of 2-100g/10min, preferably 5-100g/10min at 190℃ under a load of 2.16 kg.

~~28~~26. The method as claimed in any one of claims ~~19-27~~18-25, wherein the extrusion temperature in the step 1) is 130-190℃, preferably 150-180℃, and more preferably 160-180℃.

~~29~~27. The method as claimed in any one of claims ~~19-28~~18-26, wherein the organic peroxide is selected from dialkyl peroxides, diacyl peroxides or peroxyesters.

~~30~~28. The method as claimed in claim ~~29~~27, wherein the dialkyl peroxide is selected from dicumyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane or di(tert-butylperoxyisopropyl)benzene; the diacyl peroxide is selected from benzoyl peroxide or lauroyl peroxide.

~~31~~29. The method as claimed in any one of claims ~~19-30~~18-28, wherein the organic peroxide is used in an amount of 0.01 to 5wt% based on the amount of the branched aliphatic-aromatic copolyester.

~~32~~30. The method as claimed in any one of claims ~~19-31~~18-29, wherein the copolyester has a melt index of 0.1 to 10g/10min at 190℃ under a load of 2.16 kg.

~~33~~31. The method as claimed in any one of claims ~~19-32~~18-30, wherein the copolyester is also mixed with additives in the step 2), wherein the additives include an antioxidant, a slipping agent, an anti-blocking agent and a nucleating agent.

~~34~~32. The method as claimed in claim ~~33~~31, wherein the amount of the antioxidant is 0.05-5 parts, the amount of the slipping agent is 0.05-5 parts, the amount of the anti-blocking agent is 0.05-5 parts, and the amount of the nucleating agent is 0.1-20 parts based on 100 parts by weight of the copolyester.

~~35~~33. The method as claimed in any one of claims ~~33-34~~31-32, wherein the

antioxidant is a mixture of a hindered phenol antioxidant and a phosphite antioxidant in a mass ratio of 1: 1.

~~36~~34. The method as claimed in claim ~~35~~33, wherein the hindered phenol antioxidant is selected from antioxidant 1010, antioxidant 1076, antioxidant 245 or antioxidant 246; the phosphite antioxidant is selected from triphenyl phosphate, trimethyl phosphate or antioxidant 168.

~~37~~35. The method as claimed in any one of claims ~~33-34~~31-32, wherein the slipping agent is stearate or organic carboxylic acid amide, wherein the stearate is preferably calcium stearate, and the organic carboxylic acid amide is preferably erucamide or oleamide;

the anti-blocking agent is silica or talc;

the nucleating agent is selected from hyperbranched polyamides, low density polyethylene or ethylene-methacrylic acid ionomers.

~~38~~36. A copolyester, which is obtained by extrusion reaction of a branched aliphatic-aromatic copolyester derived from monomer a, monomer b, monomer c and monomer d with an organic peroxide, wherein the monomer a is an aromatic dibasic acid or an ester derivative thereof; the monomer b is one or more of C_2-C_{10} aliphatic dihydric alcohols or C_3-C_{10} alicyclic dihydric alcohols; the monomer c is a C_4-C_{20} aliphatic dibasic acid or an ester derivative thereof; the monomer d is one or more of polyols with a functionality of more than 2, polycarboxylic acids with a functionality of more than 2, anhydrides with a functionality of more than 2, epoxy compounds or anhydrides with hydroxyl or carboxyl group, glycidyl ester, glycidyl ether, glycidol, lactones or cyclic carbonates with hydroxyl or carboxyl side group; the branched aliphatic-aromatic copolyester is obtained by reacting monomer a, monomer b, monomer c and monomer d under the action of a catalyst system containing a

second catalyst, wherein the second catalyst is a compound of $RE(R^3)_3$, wherein RE is a rare earth metal element, R^3 is at least one selected from the group consisting of halogen, alkoxy group, aryloxy group, acetylacetone group and R^4COO- group, wherein R^4 is C_1-C_{30} alkyl group.

~~39. The copolyester as claimed in claim 38, wherein the branched aliphatic-aromatic copolyester is obtained by reacting monomer a, monomer b, monomer c and monomer d under the action of a catalyst system containing a second catalyst, wherein the second catalyst is a compound of $RE(R^3)_3$, wherein RE is a rare earth metal element, R^3 is at least one selected from the group consisting of halogen, alkoxy group, aryloxy group, acetylacetone group and R^4COO- group, wherein R^4 is C_1-C_{30} alkyl group.~~

~~40~~37. The copolyester as claimed in claim ~~39~~36, wherein, in the compound of $RE(R^3)_3$ as the second catalyst, RE is lanthanum, cerium, praseodymium, neodymium, terbium, ytterbium, dysprosium, samarium or scandium; the halogen is chlorine or bromine, the alkoxy group is C_3-C_6 alkoxy group, the aryloxy group is aryloxy group comprising at least one benzene ring and/or naphthalene ring, and R^4 is C_1-C_{20} alkyl group.

~~41~~38. The copolyester as claimed in claim ~~39~~36, wherein the catalyst system further comprises a first catalyst and/or a third catalyst; wherein the first catalyst is one or more selected from the group consisting of an oxide of M, $M(OR^1)_n$ and $M(OOCR^2)_m$, wherein M is titanium, antimony or zinc, n and m are each independently the valence of M, R^1 is C_1-C_{10} alkyl group, and R^2 is C_1-C_{20} alkyl group; the third catalyst is at least one organotin compound.

~~42~~39. The copolyester as claimed in claim ~~41~~38, wherein the molar ratio of the catalyst in its entirety to the monomer (a + c) is 1: 1000-20000, and the

molar ratio of the first catalyst to the second catalyst to the third catalyst is 0-20: 0.1-10: 0-1, preferably 0.1-20: 0.1-10: 1.

~~43~~40. The copolyester as claimed in any one of claims ~~38-42~~36-39, wherein the amounts of various monomers are as follows: the molar ratio of (a + c) to b is 1: 0.8-3, the molar ratio of (a + c) to d is 100-2000: 1, the molar ratio of a to c is 0: 100-95: 5, preferably 0: 100-60: 40.

~~44~~41. The copolyester as claimed in any one of claims ~~38-43~~36-40, wherein the monomer a is selected from terephthalic acid or dimethyl terephthalate; the monomer b is selected from ethylene glycol, 1,3-propanediol or 1,4-butanediol; the monomer c is selected from succinic acid, succinic anhydride, dimethyl succinate, adipic acid or dimethyl adipate; the monomer d is selected from pyromellitic dianhydride, glycerol, pentaerythritol, glycidyl succinate, glycidyl adipate, glycidyl terephthalate, ethylene glycol glycidyl ether, 1,4-butanediol glycidyl ether, glycidic acid, glycidol, 3-hydroxyphthalic anhydride, 4-hydroxyphthalic anhydride, 3-hydroxymethylcaprolactone, a five-membered or six-membered cyclic carbonate with an alkylhydroxy group or an alkylcarboxyl group.

~~45~~42. The copolyester as claimed in any one of claims ~~38-44~~36-41, wherein the branched aliphatic-aromatic copolyester is prepared as follows: under the action of a catalyst system, monomer a, monomer b, monomer c and monomer d are mixed for esterification or transesterification reaction, or the esterification or transesterification product of monomer a and monomer b and the esterification or transesterification product of monomer c and monomer d are mixed for copolycondensation reaction.

~~46~~43. The copolyester as claimed in any one of claims ~~38-45~~36-42,

wherein the branched aliphatic-aromatic copolyester has a melt index of 2-100g/10min, preferably 5-100g/10min at 190℃ under a load of 2.16 kg.

~~47~~44. The copolyester as claimed in any one of claims ~~38-46~~36-43, wherein the organic peroxide is selected from dialkyl peroxides, diacyl peroxides or peroxyesters.

~~48~~45. The copolyester as claimed in claim ~~47~~44, wherein the dialkyl peroxide is selected from dicumyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane or di(tert-butylperoxyisopropyl)benzene; the diacyl peroxide is selected from benzoyl peroxide or lauroyl peroxide.

~~49~~46. The copolyester as claimed in any one of claims ~~38-48~~36-45, wherein the organic peroxide is used in an amount of 0.01 to 5wt% based on the amount of the branched aliphatic-aromatic copolyester.

~~50~~47. The copolyester as claimed in any one of claims ~~38-49~~36-46, wherein the copolyester has a melt index of 0.1 to 10g/10min at 190℃ under a load of 2.16 kg.