(19) World Intellectual Property Organization

International Bureau



(43) International Publication Date 27 December 2007 (27.12.2007)

PCT

(10) International Publication Number WO 2007/149045 Al

(51) International Patent Classification:

 C08F 251/00 (2006.01)
 C08F 251/02 (2006.01)

 C08J 5/10 (2006.01)
 C12P 19/18 (2006.01)

 B29C 70/00 (2006.01)
 D06M 15/03 (2006.01)

 C08B 37/14 (2006.01)
 D06M 101/06 (2006.01)

(21) International Application Number:

PCT/SE2007/050450

(22) **International Filing Date:** 21 June 2007 (21.06.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

PCT/EP2006/006099 23 June 2006 (23.06.2006) EP

(71) Applicant (for all designated States except US): SWE-TREE TECHNOLOGIES AB [SE/SE]; Po. Box 7981, S-907 19 Umea (SE).

(72) Inventors; and

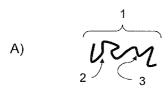
(75) Inventors/Applicants (for US only): ZHOU, Qi [CN/SE]; Nasbydalsvagen 4, S-183 31 Taby (SE). BRUMER, Harry [US/SE]; Paladergatan 39, S-121 37 Johanneshov (SE). TEERI, Tuula Tellervo [FI/SE]; Mejerfeldtsvagen 86, S-183 56 Taby (SE). STOLT, Johan Patrik [SE/SE]; Starbyvagen 193, S-262 95 Ängelholm (SE). ÖDBERG, Lars Goran [SE/SE]; Linnegatan 27, S-1 14 47 Stockholm (SE).

- (74) Agent: ALBIHNS AB; P.O. Box 5581, S-114 85 Stock-holm (SE).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, 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, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, 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,

(57) Abstract: The present invention relates to a novel group of copolymers comprising a soluble carbohydrate polymer (SCP), which typically is a non-starch car-

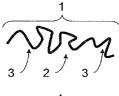
[Continued on next page]

(54) Title: COPOLYMER, MODIFIED POLYMER CARBOHYDRATE MATERIAL, MODIHED BULD POLYMER, COMPOSITE MATERIAL, AND METHODS OF PREPARATION

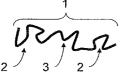


bohydrate, and a macromolecule covalently attached to the SCP. The macromolecule may e.g. be a hydrophobic copolymer, a polyelectrolyte polymer or a biodegradable polymer. The present invention furthermore relates to a method of preparing the copolymer, products comprising the copolymer, and to methods of preparing the products comprising the copolymer. The products comprising a copolymer are for example a polymeric carbohydrate material (PCM) modified by attachment of a copolymer, and a composite material comprising the modified PCM.

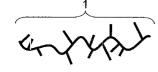




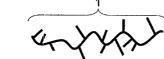














WO 2007/149045 A1



GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT,BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- with amended claims

Date of publication of the amended claims: 28 February 2008

15

35

AMENDED CLAIMS

received by the International Bureau on 26 November 2007(26.1 1.2007)

- 1. Use of a copolymer comprising a xyloglucan and a macromolecule covalently attached to the xyloglucan for modifying a polymeric carbohydrate material, especially cellulose.
- 2. The use according to claim 1, wherein the macromolecule comprises a hydrophobic polymer.
- 3. The use according to any of claims 1-2, wherein the macromolecule comprises abiodegradable polymer.
 - 4. The use according to any of the preceding claims wherein the macromolecule comprises an electrically conducting polymer polymer, which may be chosen from poly(acetylene)s, poly(pyrrole)s, poly(thiophene)s, poly(aniline)s, poly(fluorene)s, polynaphthalenes, poly(phenylene sulfide), and poly(para-phenylene vinylene)s.
 - 5. The use according to any of the preceding claims wherein the macromolecule comprises a signal-responsive polymer.
- 20 6. The use according to any of the preceding claims, wherein the copolymer is a block copolymer.
 - 7. The use according to any of the claims 1-6, wherein the copolymer is a dendrimer comprising:
- a branched macromolecule having at least 3 end groups, and at least one xyloglucan covalently attached to one of the at least 3 end groups of the branched macromolecule.
- 8. The use according to any of the preceding claims comprising in the range of 1-50030 xyloglucans covalently attached to the macromolecule.
 - 9. An aqueous formulation of the copolymer according to any of the preceding claims, wherein the aqueous formulation comprises copolymer in an amount in the range of 0.1-80% by weight, and water in an amount in the range of 20-99.9% by weight.
 - 10. The aqueous formulation according to claim 9, furthermore comprising an organic, water soluble solvent, such as in an amount in the range of 5-45% by weight.

- 11. The aqueous formulation according to any of the claims 9-10, wherein the organic, water soluble solvent comprises an alcohol, acetone, propylene glycol, or glycerol, or a mixture thereof
- 5 12. The aqueous formulation according to any of the claims 9-11, furthermore comprising an emulsifier such as in an amount in the range of 0.1-10% by weight.
 - 13. A hydrophobic formulation of the copolymer according to any of the claims 1-8, wherein the hydrophobic formulation comprises copolymer in an amount in the range of 0.1-80% by weight, and a hydrophobic solvent in an amount in the range of 20-99.9% by weight.
 - 14. A dry formulation of the copolymer according to any of the claims 1-8, wherein the dry formulation comprises copolymer in an amount in the range of 5-99.9% by weight, and water in an amount in the range of 0.1-10% by weight, preferably in the range of 0.1-5% by weight, and even more preferably in the range of 0.1-2% by weight.
 - 15. The dry formulation according to claim 10, furthermore comprising a wetting agent, and/or a humectant, and/or an anti-agglomeration agent
- 20 16. A method of preparing a copolymer according to any of the preceding claims, the method comprising the steps of
 - a) providing an xyloglucan and a macromolecule, and

15

25

40

b) attaching the macromolecule covalently to the X xyloglucan.

wherein step b) may involve one or more processes selected from the group consisting of:

- reacting the xyloglucan with galactose oxidase;
- reacting the xyloglucan with an oxidizing agent,
- oxidizing of a primary alcohol group to obtain an aldehyde group; and
- reacting an aldehyde group with a primary amino group.
- 30 17. The method according to claim 16, wherein step b) involves reductive amination of the xyloglucan, wherein the xyloglucan may comprise an amino group and wherein the macromolecule, such as the hydrophobic polymer, may comprise an aldehyde group, and step b) involves reacting the aldehyde group with the amino group or wherein xyloglucan comprises an aldehyde group and the macromolecule comprises an amino group, and step b) involves reacting the aldehyde group with the amino group.
 - 18. The method according to any of the claims 16-17, wherein the macromolecule comprises an aldehyde group and step b) involves reacting a xyloglucan with a diamine compound and a reducing agent to obtain an aminated xyloglucan and to react the aminated xyloglucan with macromolecule comprising the aldehyde group to obtain the copolymer.

- 19. The method according to claim 18, wherein the reducing agent is a salt of cyanoborohydride.
- 5 20. A method of preparing a copolymer according to any of the preceding claims, the method comprising the steps of
 - a) providing an xyloglucan,

20

25

30

35

- b) attaching covalently a polymerisation initiator to the xyloglucan, wherein at least 2 polymerisation initiators may be attached to the xyloglucan or wherein the polymerisation initiator may be selected from the group consisting of an acid-containing initiator, an allyl bromide, an allyl chloride, and a phenolic ester based monofunctional initiators,
- c) polymerising onto the xyloglucan via the polymerisation initiator.
- 21. A modified polymeric carbohydrate material (PCM) comprising a copolymer according to any of the claims 1-8, wherein the weight ratio between copolymer and PCM is in the range of 100:1 1:100, such as in the range of 100:1 1:1, e.g. in the range of 1:1 1:100.
 - 22. A method of preparing a modified hydrophobic bulk polymer, the method comprising the steps of

1) providing a copolymer according to any of the preceding claims ..., said copolymer comprising an xyloglucan and a hydrophobic polymer,

2) binding the copolymer to a hydrophobic bulk polymer under suitable conditions, thus obtaining the modified hydrophobic bulk polymer.

23. A modified hydrophobic bulk polymer comprising a hydrophobic bulk polymer and a copolymer according to any of the claims 1-8, wherein the weight ratio between copolymer and hydrophobic bulk polymer may be in the range of 10:1 - 1:1000.

24. A method of preparing a composite material comprising a hydrophobic bulk polymer and PCM, the method comprising the steps of:

- i) providing a hydrophobic bulk polymer and a modified PCM according to claim 21 and
- ii) mixing the hydrophobic bulk polymer and the modified PCM.
- 25. A method of preparing a composite material comprising a hydrophobic bulk polymer and PCM, the method comprising the steps of:
- i) providing a PCM and a modified hydrophobic bulk polymer according to claim 23,
- 40 ii) mixing the modified hydrophobic bulk polymer and the PCM.

- 26. A method of preparing a composite material comprising a hydrophobic bulk polymer and PCM, the method comprising the steps of:
 - i) providing a PCM, a hydrophobic bulk polymer, and a copolymer according to any of claims 1-8.
 - ii) mixing the modified hydrophobic bulk polymer and the PCM.
- 27. A composite material comprising a PCM and the modified hydrophobic bulk polymer according to claim 23 or obtainable by a method according to any of the claims 24-26.
 - 28. Use of the copolymer according to any of the claims 1-8 as a compatibiliser, whereby the at least one macromolecule of the copolymer may be a hydrophobic polymer.
- 29. A copolymer comprising a xyloglucan and a macromolecule covalently attached to the xyloglucan, wherein the macromolecule comprises an electrically conducting polymer.
 - 30. A copolymer comprising a xyloglucan and a macromolecule covalently attached to the xyloglucan, wherein the copolymer is a dendrimer comprising:
- a branched macromolecule having at least 3 end groups, and at least one SCP covalently attached to one of the at least 3 end groups of the branched macromolecule.