AMPHIPHILIC GRAFT COPOLYMER FOR WATERBORNE SHAPE MEMORY COATINGS

A waterborne shape memory polymer coating that gives textiles and fibers good shape memory performance. An amphiphilic, crosslinkable grafted polysaccharide polymer was synthesized and provided in a water dispersion that can be applied to a flexible fibrous material and then crosslinked to yield good shape memory properties. The polymer coating showed good binding to human hair, which could be styled into a permanent shape (e.g., straight) during the crosslinked step. Next, this permanent shape can be styled to a temporary shape (e.g., curly) by heating and styling, and cooling. Finally, the permanent style can be regained by activation with water, heat, or both.
TITLE
AMPHOPHILIC GRAFT COPOLYMER FOR WATERBORNE SHAPE MEMORY COATINGS
CROSS-REFERENCE TO RELATED APPLICATIONS
[0001] The present application claims priority to U.S. Provisional No. 61/781,18, filed on March 14, 2014.
BACKGROUND OF THE INVENTION
1. FIELD OF THE INVENTION
[0002] The present invention relates to fiber coating and, more particularly, to a shape memory polymer coating for hair and other fibers.
2. DESCRIPTION OF THE RELATED ART
[0003] Polymeric coatings have been used in a wide range of application fields such as automobiles, beauty products, and medical devices. Among the existing hair styling products (gels, sprays, etc) and fabric coatings (e.g., starch), a big disadvantage is that they do not enable reversible styling, or "re-styling", with two styles in memory. Thus, a need exits for the styling products with good shape memory properties and good hair or fabric binding ability.
[0004] Shape memory materials are those materials that have the ability to "memorize" a macroscopic (permanent) shape, be manipulated and "fixed" to a temporary and dormant shape under specific conditions of temperature and stress, and then later recover to the original, stress-free, condition under thermal, electrical, or environmental command. This recovery is associated with elastic deformation stored during prior manipulation. Shape memory materials have aroused great attention by scientists and engineers due to their capacity to remember two shapes at different conditions. This gives materials great potential for sensors, actuators, smart devices of great potential for applications that range from consumer products to sporting goods and medical devices. The most prominent and widely used shape memory materials currently are shape memory alloys (SMAs). Their shape memory effect comes from the existence of two stable crystal structures: the high temperature-favored austenitic phase and low temperature-favored (and "yield-able") martensitic phase. Downsides that limit their application exist, including limited recoverable strains less than 8%, inherently high stiffness, high cost, comparatively inflexible transition temperature, and demanding processing and training conditions. Such limitations have provided motivation for the development of alternative materials, especially
shape memory properties, the good binding abilities, and the intrinsic nature (non-tacky, odorless, etc) make these materials good candidates for applications as coatings on flexible substrates, such as hair, fabric, paper, sails, plastic film, among others.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING(S)

[0009] The present invention will be more fully understood and appreciated by reading the following Detailed Description in conjunction with the accompanying drawings, in which:

[0010] Figure 1 is a schematic showing the macromolecular design for waterborne SMP.

[0011] Figure 2 is a series of chemical diagrams showing the synthesis of: (a) PCL initiated by benzyl alcohol; (b) Monocarboxy-capped PCL (PCL-COOH); (c) phthloychitosan (PHCS); (d) graft copolymers (PHCS-g-PCL); and (e) CS-g-PCL by deprotecting PHCS-g-PCL.

[0012] Figure 3 is a series of photographs showing: (a) CS-g-PCL obtained as a yellow powdery material from the synthesis steps shown in Figure 2; and (b) Aqueous dispersion (2%, w/v) of the CS-g-PCL in 1% acetic acid aqueous solution (pH 2.8) under stirring for 24 hours.

[0013] Figure 4 is a series of photographs illustrating the shape memory behaviors of CS-g-PCL coated hair tresses, crosslinked with BDGE for: (a) permanent shapes (L_p); (b) deformed shapes after being deformed at 60 °C and cooled and fixed for 10 min at -20 °C (L_d); (c) temporary shapes after hanging at room temperature (L_t); (d) recovered shapes after heated at 60 °C (L_r), where Sample (1) is the coating having a permanent shape as straight and sample (2) is the coating having a permanent shape as curly.

DETAILED DESCRIPTION OF THE INVENTION

[0014] Referring now to the drawings, wherein like reference numerals refer to like parts throughout, the present invention comprises the synthesis of a graft copolymer and the preparation of aqueous dispersion and shape memory testing on hair tresses to provide soft SMPs that are waterborne and gain their softness from a combination of composition and architecture. More specifically, the present invention comprises a graft copolymer approach in which the polymer backbone is a positively charged, water-soluble polysaccharide (chitosan) and the grafting chains are oligomeric, hydrophobic chains capable of crystallizing for a temporary shape.

[0015] Referring to Figure 1, the permanent shape for such a graft copolymer is established by chemical crosslinking during styling. The poly(ε-caprolactone) (PCL) grafts serve for temporary shape setting. Covalent crosslinking is responsible for setting the permanent shape
polymeric shape memory materials. Polymeric materials offer intrinsic potential for a shape memory effect, although the mechanisms responsible differ dramatically from those of metal alloys. In SMAs, pseudoplastic fixing is possible through the martensitic de-twinning mechanism, while recovery is triggered by the martensite-austenite phase transition.

[0005] In contrast, shape memory polymers (SMPs) achieve temporary strain fixing and recovery through a variety of physical means, while the underlying extensibility is derived from the intrinsic elasticity of polymeric networks. Most shape memory polymers are stiff at temperatures below activation. This is due to the fact that crystallization or vitrification (glass formation) of the entire polymeric materials has been utilized as the means to allow strain fixing. As a consequence, SMPs have not been amenable to applications commonly served by elastomers, such as seals, conformal textiles, among others.

BRIEF SUMMARY OF THE INVENTION

[0006] The present invention comprises systems and method to synthesize and test new polymer designs suitable for applications such as waterborne coating products for hair or fabric, or any flexible substrate (hereafter "substrates") engendering shape memory attributes to those substrates.

[0007] More particularly, the present invention encompasses a family of new polymer designs centered around use of a natural polymer has been conceived in modular fashion and with a "graft copolymer" architecture. In particular, a graft copolymer is prepared following an approach in which the polymer backbone is a positively charged, water-soluble polysaccharide (deacetylated chitosan) and the grafting chains are oligomeric, hydrophobic chains (in a preferred embodiment, poly(e-caprolactone)) capable of crystallizing for a temporary shape. The permanent shape for such a graft copolymer is established by chemical crosslinking during styling or otherwise forming. The chitosan backbone, once quaternized, is positively charged and allows water dispersion via micellization along with binding to negative charges on hair or other natural fibers. Shape memory properties of the polymer coatings were tested on hair tresses and demonstrated to be quite promising.

[0008] With these characteristics of the present invention, a consumer can apply the polymer from aqueous dispersion and then style the permanent shape (e.g., straightening) at a relatively low temperature (60 °C). Next, the permanent shape can be altered to curly by styling at that temperature. Finally, the permanent style can be regained by heat activation. The good
and the PCL grafts are capable of crystallizing for a temporary shape. The chitosan backbone, once quaternized, will be positively charged and allow water dispersion via micellization along with binding to negative charges on hair. Both chitosan and the PCL - polymers encompassed by the present invention - are known to be non-toxic and have been widely studied for their applications in pharmaceutical, cosmetics, biomedical, agricultural, and food industries.

[0016] The graft copolymers of chitosan with PCL are prepared via a protection-graft-deprotection route, by the esterification of phthaloyl-protected chitosan (PHCS) with PCL-COOH. Following that phthaloyl groups are deprotected to give the free amino groups. In this way, good control over the molecular weight of the grafting chains (PCL) is possible. The synthetic strategy to make the graft copolymer (CS-g-PCL) may be seen in Figure 2, which shows the synthesis of: (a) PCL initiated by benzyl alcohol; (b) Monocarboxy-capped PCL (PCL-COOH); (c) phthloychitosan (PHCS); (d) graft copolymers (PHCS-g-PCL); and (e) CS-g-PCL by deprotecting PHCS-g-PCL. The final products (CS-g-PCL) are yellow powdery materials, as seen in Figure 3(a). The thermal behavior of the graft copolymer was characterized by differential scanning calorimetry (DSC). A melting transition was observed around 50 °C, indicating successful grafting of PCL chains onto the chitosan backbone.

[0017] The graft copolymer (CS-g-PCL5k) was then dispersed in 1% acetic acid (a good solvent for deacetylated chitosan, but poor solvent for PCL grafts) under stirring for 24 hours to obtain the water dispersion. The size of self-aggregates and their distribution were measured using a Malver Instrument Zetasizer Nano S laser scattering system. The mean diameters of aggregates range from 200 to 400 nm, with a unimodal size distribution. The resulting dispersion is shown in Figure 3(b).

[0018] Dark brown hair tresses were with average weight of 2 grams were used to test the present invention. Hair tresses were coated with 4 ml aqueous dispersion (polymer: ~40 mg/g of hair) using a pipette and dried in the hood at RT. Dimethyl 3-3, dithio bis' propionimidate (DTBP), together with two diepoxide-based bifunctional linkers, neopentyl glycol diglycidyl ether (NGDE) and 1,4-butanediol diglycidyl ether (BDGE) were used to crosslink the chitosan chains via the reactive amino group on the chitosan backbone. Other diepoxide molecules may serve as suitable crosslinkers. The permanent shapes were set to be either straight or curly at this step. The crosslinker solution was applied onto the hairs and crosslinked at room temperature for 24 hours. The amount of crosslinking solution applied for
different crosslinkers were shown in Table 1 below. It was noted that hair tresses coated with copolymer dispersion felt soft and can easily be combed through.

**Table 1.** The amount of crosslinking solution applied for different crosslinkers.

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<tr>
<th>Crosslinker</th>
<th>Applied Amount</th>
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<tr>
<td>DTBP</td>
<td>0.5 wt% DTBP in 6ml Tris buffer</td>
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<tr>
<td>NGDE</td>
<td>2.5 ml NGDE + 2.5 ml isopropanol</td>
</tr>
<tr>
<td>BDGE</td>
<td>0.8 ml BDGE + 1.6 ml H$_2$O</td>
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</table>

Shape memory properties of the polymer coating were investigated on hair tresses. The length of the permanent shape was recorded as $L_p$. Hair tresses were deformed by either hanging a weight (straight as temporary shape) or by wrapping around a plastic rod (curly as temporary shape) at 60 °C. Samples were then transferred to a freezer (-20 °C) for 10 min to allow the crystallization of PCL phases. Then the load was removed, and the samples’ lengths were measured ($L_d$). Shape fixing ability was evaluated by hanging samples at room temperature for 30 min, and the length of the tresses at the end of this stage were measured ($L_i$). Finally, shape recovery was induced by hanging tresses at 60 °C for 10 min to a recovered length, $L_r$.

The fixing ($R_f$) and recovery ($R_r$) ratios were calculated for each sample using Equations 1 and 2:

$$R_f(\%) = \left(\frac{L_i - L_p}{L_d - L_p}\right) \times 100 \quad (1)$$

$$R_r(\%) = \left(\frac{L_r - L_i}{L_p - L_i}\right) \times 100 \quad (2)$$

The tress crosslinked with DTBP showed moderate recovery behavior with $R_r$ of 75 % when the permanent shape was programmed to be straight. However, in this case the fixing ratio was low ($R_f = 45$%). When setting the permanent shape as curly, the recovery ability ($R_r$) decreased to 15%, while preached 100%. The different fixing and recovery behaviors of these two scenarios were attributed to the effect of gravity. After switching the crosslinker from DTBP to the two diepoxide-based bifunctional linkers (i.e. NGDE and BDGE), the recovery ratios significantly improved to 46% and 97% for permanent straight shape and permanent curly shape, respectively, indicating higher crosslinking density was achieved.
Referring to Figure 4, the shape memory behaviors of CS-g-PCL coated hair tresses, crosslinked with BDGE, may be seen as follows: (a) permanent shapes \( (L_p) \); (b) deformed shapes after being deformed at 60 °C and cooled and fixed for 10 min at -20 °C \( (L_d) \); (c) temporary shapes after hanging at room temperature \( (L_t) \); (d) recovered shapes after heated at 60 °C \( (L_r) \), where Sample (1) is permanent shape as straight and sample (2) is permanent shape as curly.

The present invention could be used as a coating on flexible substrates, including hair, human skin, fabric, paper, sails, plastic film, botanical plant leaves, wire, monofilament, thread, yarn, elastomer (rubber), among others.
CLAIMS

What is claimed is:

1. A graft polymer coating, comprising:
   a polymer backbone comprising a water soluble polysaccharide; and
   a side chain comprising a hydrophobic oligomer grafted onto said polymer backbone.

2. The coating of claim 1, wherein said water soluble polysaccharide is positively charged.

3. The coating of claim 2, wherein said water soluble polysaccharide comprises chitosan.

4. The coating of claim 1, wherein said grafting chain comprises poly(ɛ-caprolactone).

5. The coating of claim 1, wherein said polymer backbone and said grafting chain are dispersed in water via micellization.

6. The coating of claim 1, wherein said polymer backbone is covalently crosslinked.

7. The coating of claim 6, wherein said melting transition temperature is about 50 °C.

8. A method of providing shape memory to fibers, comprising the steps of:
   coating an aqueous dispersion of a polymer backbone comprising a water soluble polysaccharide and a side chain comprising a hydrophobic oligomer grafted onto said polymer backbone onto at least one fiber; and
   applying a cross-linker solution to crosslink the polymer backbone.

9. The method of claim 8, wherein the cross-linker is selected from the group consisting of dimethyl 3-3, dithio bis’ propionimidate (DTBP), neopentyl glycol diglycidyl ether (NGDE), and 1,4-butanediol diglycidyl ether (BDGE).

10. The method of claim 8, wherein said water soluble polysaccharide is positively charged.

11. The method of claim 10, wherein said water soluble polysaccharide comprises chitosan.

12. The method of claim 8, wherein said grafting chain comprises poly(ɛ-caprolactone).
13. The method of claim 8, wherein said aqueous dispersion comprises said polymer backbone and said grafting chain dispersed in water via micellization.

14. The method of claim 8, wherein said melting transition temperature is about 50 °C.

15. The method of claim 8, further comprising the step of arranging said at least one fiber into a first predetermined configuration prior to cross-linked said polymer backbone.

16. The method of claim 15, further comprising the step of arranging said at least one fiber into a second, different predetermined configuration after cross-linking said polymer backbone.

17. The method of claim 16, further comprising the step of returning said coated fiber to said first predetermined configuration from said second predetermined configuration.

18. The method of claim 17, wherein said step of returning said coated fiber to said first predetermined configuration comprises heating said at least one fiber.
FIGURE 2
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
C09D 101/00(2006.01)i, C09D 201/02(2006.01)i

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)
C09D 101/00; C09G 63/02; C09D 201/02

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic database consulted during the international search (name of database and, where practicable, search terms used)
eKOMPASS (KIPO internal)

& Keywords: graft polymer, shape memory, backbone, water soluble polysaccharide, chitosan, side chain, hydrophobic oligomer, polycaprolactone

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>A</td>
<td>See abstract; See p. 241, right column, lines 1-7; schemes 2-3</td>
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<td>X</td>
<td>LIU, LI et al., 'Preparation of chitosan-polyacrylamidactone copolymers through ring-opening polymerization of epsilon-caprolactone and chitosan', Biopolymer, 28 April 2005, Vol. 78, pp. 163-170</td>
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<td>See abstract; p. 163, left column; scheme 1</td>
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<td>LIU, LI et al., 'Synthesis and characterization of chitosan-graft-polycaprolactone copolymers', European Polymer Journal, 09 September 2004, Vol. 40, pp. 2739-3744</td>
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<td>A</td>
<td>See abstract; p. 2740; scheme 2</td>
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<td>A</td>
<td>GU, XINZHU et al., 'Entangled-based shape memory polyurethanes: syntheses and characterization', Polymer, 08 October 2012, Vol. 53, pp. 5924-5934</td>
<td>1-6, 8-13 ,15-18</td>
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<tr>
<td></td>
<td>See abstract</td>
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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 raise 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 August 2014 (26.08.2014)

Date of mailing of the international search report
26 August 2014 (26.08.2014)

Name and mailing address of the ISA/KR

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Authorized officer
HONG, Sung Ran
Telephone No. +82-42-481-5405

Form PCT/ISA/210 (second sheet) (July 2009)
**INTERNATIONAL SEARCH REPORT**

**DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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<tr>
<td>A</td>
<td>US 6160084 A (LANGER, ROBERT S. et al.) 12 December 2000 See claims 1, 9-10</td>
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INTERNATIONAL SEARCH REPORT

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.: 7, 14
   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:
   Claims 7, 14 are worded in reference to 'melting transition temperature' of claims 6, 8 respectively. However, said 'melting transition temperature' has not been worded in claims 6, 8.

3. ☐ Claims Nos.:
   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 an additional fees, this Authority did not invite payment of any 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.

Form PCT/ISA/210 (continuation of first sheet (2)) (July 2009)
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