MULTIGRAFT COPOLYMERS AS SUPERELASTOMERS

TECHNICAL FIELD

Elastomers comprising multigraft copolymers having randomly spaced branch points, for example comprising a polydiene backbone and randomly spaced polystyrene grafts, are described. Also described are methods of synthesizing and characterizing the copolymers. The copolymers can be used as superelastomers, for example, in adhesives and/or as components in a variety of products, including medical implants.

BACKGROUND

Thermoplastic elastomers (TPEs) represent an important segment of the worldwide elastomer market due to their combination of mechanical properties comparable to vulcanized rubbers and straightforward processing similar to that of thermoplastics. See Legge et al., Thermoplastic Elastomers, Munich: Hanser, 1987. TPEs are also of interest because of their capacity to self-assemble to form ordered phase separated structures having nanoscale dimensions, with morphologies and properties tunable by controlling the volume fractions of hard and soft segments. See Rader, C.P., in Modern Plastics Encyclopedia, Volume 72, New York: McGraw-Hill, 1996.

Linear ABA triblock copolymers, including styrenic block copolymers (SBC), are often usable as TPEs. The SBCs include, for example, the SIS and SBS triblock copolymers, where S represents glassy polystyrene (PS) end-blocks and I and B represent rubbery polyisoprene (PI) and polybutadiene (PBD) mid-blocks, respectively. Some of these copolymers are sold under the trade name KRATON™ (Kraton Polymers, Houston, Texas, United States of America). For these block copolymers, the morphology formed, and thus the mechanical properties, are directly linked to the volume fractions of the two components.

Star block copolymers, *e.g.*, star polymers where each arm is a block copolymer, having PS outer blocks and PI inner blocks, have been reported as having improved tensile strength relative to linear triblocks of comparable composition and segment molecular weights. See Bi and Fetters, *Macromolecules*,

9, 732-742 (1976). Commercial star block copolymers based on S/I and S/B compositions have been commercialized by companies such as the Phillips Petroleum Company (now part of ConocoPhillips Company, Houston, Texas, United States of America), and BASF (Ludwigshafen, Germany).

Graft copolymers comprising PI backbones and regularly spaced PS side chains attached to the backbone at branch points have also been shown to have elastomeric properties. See, *e.g.*, Uhrig and Mays, *Macromolecules*, 35, 7182-7190 (2002); and Mays et al., *Macromol. Symp.*, 215, 111-126 (2004). However, the synthesis of regular spaced copolymers can be challenging. See Uhrig and Mays, *Macromolecules*, 35, 7182-7190 (2002).

Accordingly, there is need in the art for additional elastomeric polymers and materials that can be produced therefrom, that can be synthesized easily and at low cost. There is also a continuing need for elastomeric polymers that have mechanical properties that can be readily fine-tuned particular end uses.

SUMMARY

In one aspect, the present disclosure refers to a thermoplastic elastomer composition comprising: a random multigraft copolymer comprising: a rubbery polymeric backbone comprising a plurality of randomly spaced branch points, wherein the rubbery polymeric backbone comprises polyisoprene, hydrogenated polyisoprene, polybutadiene, hydrogenated polybutadiene, polyisobutylene, acrylic rubber, or combinations thereof; and a plurality of glassy or semi-crystalline polymeric grafts comprising polystyrene, poly(α-methylstyrene) or another glassy styrenic polymer, polymethylmethacrylate or another glassy acrylic polymer, or combinations thereof, and wherein each of the plurality of glassy or semi-crystalline polymeric grafts is attached to the rubbery polymeric backbone at one of the plurality of randomly spaced branch points; and wherein the random multigraft copolymer has a weight average molecular weight of about 400,000 or more, a volume fraction of glassy or semi-crystalline polymeric graft between about 14% and about 26%, and a strain at break of 1300% or greater.

In another aspect, the present disclosure refers to a fabricated article comprising the thermoplastic elastomer composition as described herein. In yet

aspect, the present disclosure refers to an adhesive comprising: a random multigraft copolymer comprising: a rubbery polymeric backbone comprising a plurality of randomly spaced branch points, wherein the rubbery polymeric backbone comprises polyisoprene, hydrogenated polyisoprene, polybutadiene, hydrogenated polybutadiene, polyisobutylene, acylic rubber, or combinations thereof; and a plurality of glassy or semi-crystalline polymeric grafts comprising polystyrene, poly(α-methylstyrene) or another glassy styrenic polymer, polymethylmethacrylate or another glassy acrylic polymer, or combinations thereof, and wherein each of the plurality of glassy or semi-crystalline polymeric grafts is attached to the rubbery polymeric backbone at one of the plurality of randomly spaced branch points; and wherein the random multigraft copolymer has a weight average molecular weight of about 400,000 or more, a volume fraction of glassy polymeric graft between about 14% and about 26%, and a strain at break of 1300% or greater; and a tackifier.

In yet another aspect, the present disclosure refers to a coated object comprising a coating layer wherein the coating layer comprises the random multigraft copolymer as described herein, wherein the coating layer covers at least a portion of a surface of a wood, ceramic, glass, carbon fiber, metal, metallic, leather, fabric, stone, or plastic object.

In still another aspect, the present disclosure refers to a thermoplastic elastomer composition comprising: a random multigraft copolymer comprising: a rubbery polymeric backbone comprising a plurality of randomly spaced branch points; and a plurality of glassy or semi-crystalline polymeric grafts, wherein each of the plurality of glassy or semi-crystalline polymeric grafts is attached to the rubbery polymeric backbone at one of the plurality of randomly spaced branch points; and wherein the random multigraft copolymer has a weight average molecular weight of about 400,000 or more, a volume fraction of glassy polymeric graft between about 14% and about 26%, and a strain at break of 1300% or greater.

In some examples, the presently disclosed subject matter provides a thermoplastic elastomer composition comprising a random multigraft copolymer comprising a rubbery polymeric backbone and a plurality of glassy polymeric grafts, wherein each of the plurality of glassy polymeric grafts is attached to the rubbery polymeric backbone at one of a plurality of randomly spaced branch points. In some

examples, the composition further comprises at least one additional component selected from the group comprising an organic filler, an inorganic filler, a wax, a tackifier, a plasticizer, an anti-oxidant, a stabilizer, a decorative agent, a biocide, a flame retardant, an anti-static agent, a therapeutic agent and combinations thereof. In some examples, the decorative agent is a pigment or a dye.

In some examples, the random multigraft copolymer has a residual strain of about 55% or less at an applied strain of about 500% or more. In some examples, the random multigraft copolymer has a residual strain of about 40% or less at an applied strain of about 300% or more.

In some examples, the random multigraft copolymer has a strain at break of 1200% or greater. In some examples, the random multigraft copolymer has a strain at break of at least 1500%.

In some examples, the random multigraft copolymer has a percent strain at break that increases linearly with the number of branch points. In some examples, the random multigraft copolymer comprises an architecture selected from the group comprising a trifunctional comb architecture, a tetrafunctional centipede architecture, and a hexafunctional barbwire architecture.

In some examples, the rubbery polymeric backbone comprises a polymeric material selected from the group comprising polyisoprene, hydrogenated polyisoprene, polybutadiene, hydrogenated polybutadiene, polyisobutylene, butyl rubber, poly(butadiene-co-acrylonitrile), a silicone rubber (*e.g.*, polydimethylsiloxane or another siloxane polymer), acrylic rubber, polychloroprene, ethylene propylene copolymer, ethylene/acrylic elastomer, urethane rubber, and combinations thereof. In some examples, the glassy polymeric grafts comprise a polymer selected from the group comprising polystyrene, hydrogenated polystyrene, poly(α-methylstyrene) or another glassy styrenic polymer or hydrogenated derivative thereof, polyethylene, urethane hard domain, polyester, polymethylmethacrylate or another glassy acrylic polymer, polyvinyl chloride, poly(vinylpyridine), polycarbonate, nylon, polyethylene terephthalate, polycyclohexadiene, hydrogenated polycyclohexadiene, and combinations thereof. In some examples, the rubbery polymeric material is polyisoprene and the glassy polymeric material is polystyrene.

In some examples, the random multigraft copolymer has a volume fraction of glassy polymeric grafts of between about 10% and about 50%. In some examples, the volume fraction of glassy polymeric grafts is between about 14% and about 26%. In some examples, the random multigraft copolymer comprises at least three branch points. In some examples, the random multigraft copolymer has a molecular weight of between about 400,000 and about 600,000.

In some examples, the presently disclosed subject matter provides a fabricated article comprising a thermoplastic elastomer composition comprising a random multigraft copolymer comprising a rubbery polymeric backbone and a plurality of glassy polymeric grafts, wherein each of the plurality of glassy polymeric grafts is attached to the rubbery polymeric backbone at one of a plurality of randomly spaced branch points. In some examples, the fabricated article is prepared by injection molding, compression molding, extrusion, or calendaring.

In some examples, the fabricated article is selected from the group comprising automotive interior or exterior parts, shoe soles or other shoe parts, elastic waistbands, diaper backings or attachments, adhesive tapes, membranes, balloons, bags, tubing, roofing tiles, medical devices, and electronic wiring coatings or other electronic device components. In some examples, the fabricated article is a medical device selected from a balloon catheter and a stent. In some examples, the article is a balloon catheter, wherein at least the inflatable portion of the balloon catheter comprises the thermoplastic elastomer composition.

In some examples, the presently disclosed subject matter provides an adhesive comprising: a random multigraft copolymer comprising a rubbery polymeric backbone and a plurality of glassy polymeric grafts, wherein each of the plurality of glassy polymeric grafts is attached to the rubbery polymeric backbone at one of a plurality of randomly spaced branch points; and a tackifier. In some examples, the adhesive is a pressure sensitive adhesive or a hot melt adhesive.

In some examples, the tackifier is selected from the group comprising rosins and derivatives thereof, terpenes, modified terpenes, an aliphatic resin, a cycloaliphatic resin, an aromatic resin, a hydrogenated hydrocarbon resin, a terpene-phenol resin, and mixtures thereof. In some examples, the adhesive further comprises one or more additives selected from the group comprising waxes,

plasticizers, anti-oxidants, stabilizers, decorative agents, biocides, flame retardants, anti-static agents, and fillers. In some examples, the decorative agent is a pigment, a dye or glitter.

In some examples, the presently disclosed subject matter provides a coated object comprising a coating layer comprising a random graft copolymer, wherein the random multigraft copolymer comprises a rubbery polymeric backbone and a plurality of glassy polymeric grafts, wherein each of the plurality of glassy polymeric grafts is attached to the rubbery polymeric backbone at one of a plurality of randomly spaced branch points, wherein the coating layer covers at least a portion of a surface of a wood, ceramic, glass, carbon fiber, metal, metallic, leather, fabric, stone, or plastic object. In some examples, the object is selected from the group comprising an article of clothing, an eating/cooking utensil, a medical implant, a medical/surgical tool, and an electronic device.

In some examples, the object is a medical implant or a medical/surgical tool and the coating layer further comprises a therapeutic agent additive selected from the group comprising a carcinostatic, an immunosuppressive, an antibiotic, an antirheumatic, an antithrombotic, an antihyperlipidemic, an ACE inhibitor, a calcium antagonist, an integrin inhibitor, an antiallergic, an antioxidant, a GPIIb/IIIa antagonist, a retinoid, a flavonoid, a carotenoid, a lipid improving agent, a DNA synthesis inhibitor, a tyrosine kinase inhibitor, an antiplatelet, a vascular smooth muscle antiproliferative agent, an anti-inflammatory agent, an interferon, and a NO production accelerator. In some examples, the coated object comprises a stent, wherein the stent comprises metal or metallic wire mesh or a metal or metallic coil having a cylindrical shape, wherein the wire mesh or coil is covered by the coating layer.

It is an object of the presently disclosed subject matter to provide random multigraft copolymers having elastomeric properties and articles comprising the copolymers.

An object of the presently disclosed subject matter having been stated hereinabove, and which is achieved in whole or in part by the presently disclosed

subject matter, other objects will become evident as the description proceeds when taken in connection with the accompanying drawings as best described hereinbelow.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A is a schematic drawing showing the molecular architecture of miktoarm star copolymers comprising two types of block material, A and B.

Fig. 1B is a schematic drawing showing the molecular architectures of regular multigraft copolymers having rubbery polymer backbones and glassy polymer side chains. The copolymer architectures include a trifunctional "comb" architecture, a tetrafunctional "centipede" architecture, and a hexafunctional "barbwire" architecture.

Fig. 1C is a schematic drawing showing the molecular architecture of random multigraft copolymers having rubbery polymer backbones and glassy polymer side chains. The copolymer architectures include a trifunctional "comb" architecture, a tetrafunctional "centipede" architecture, and a hexafunctional "barbwire" architecture.

CLAIMS

What is claimed is:

1. A thermoplastic elastomer composition comprising:

a random multigraft copolymer comprising:

a rubbery polymeric backbone comprising a plurality of randomly spaced branch points, wherein the rubbery polymeric backbone comprises polyisoprene, hydrogenated polyisoprene, polybutadiene, hydrogenated polybutadiene, polyisobutylene, acrylic rubber, or combinations thereof; and

a plurality of glassy or semi-crystalline polymeric grafts comprising polystyrene, poly(α-methylstyrene) or another glassy styrenic polymer, polymethylmethacrylate or another glassy acrylic polymer, or combinations thereof, and

wherein each of the plurality of glassy or semi-crystalline polymeric grafts is attached to the rubbery polymeric backbone at one of the plurality of randomly spaced branch points; and wherein the random multigraft copolymer has a weight average molecular weight of about 400,000 or more, a volume fraction of glassy or semi-crystalline polymeric graft between about 14% and about 26%, and a strain at break of 1300% or greater.

2. The composition of claim 1, further comprising at least one additional component selected from an organic filler, an inorganic filler, a wax, a tackifier, a plasticizer, an anti-oxidant, a stabilizer, a decorative agent, a biocide, a flame retardant, an anti-static agent, a therapeutic agent or combinations thereof.

3. The composition of claim 2, wherein the decorative agent is a pigment or a dye.

4. The composition of claim 1, wherein the random multigraft copolymer has a residual strain of about 55% or less at an applied strain of about 500% or more.

5. The composition of claim 1, wherein the random multigraft copolymer has a residual strain of about 40% or less at an applied strain of about 300% or more.

6. The composition of claim 1, wherein the random multigraft copolymer has a strain at break of at least 1500%.

7. The composition of claim 1, wherein the random multigraft copolymer has a percent strain at break that increases linearly with the number of branch points.

8. The composition of claim 1, wherein the random multigraft copolymer comprises an architecture selected from a trifunctional comb architecture, a tetrafunctional centipede architecture, or a hexafunctional barbwire architecture.

9. The composition of claim 1, wherein the random multigraft copolymer comprises at least three branch points.

10. The composition of claim 1, wherein the random multigraft copolymer has a weight average molecular weight of between about 400,000 and about 600,000.

11. A fabricated article comprising the thermoplastic elastomer composition of claim 1.

12. The fabricated article of claim 11, wherein the article is prepared by injection molding, compression molding, extrusion, or calendering.

13. The article of claim 11, wherein the article comprises automotive interior or exterior parts, shoe soles or other shoe parts, elastic waistbands, diaper

backings or attachments, adhesive tapes, membranes, balloons, bags, tubing, roofing tiles, medical devices, electronic wiring coatings, or electronic device components.

14. The article of claim 13, wherein the article is a medical device selected from a balloon catheter or a stent.

15. The article of claim 14, wherein the article is a balloon catheter, and wherein at least the inflatable portion of the balloon catheter comprises the thermoplastic elastomer composition.

16. An adhesive comprising:

a random multigraft copolymer comprising:

a rubbery polymeric backbone comprising a plurality of randomly spaced branch points, wherein the rubbery polymeric backbone comprises polyisoprene, hydrogenated polyisoprene, polybutadiene, hydrogenated polybutadiene, polyisobutylene, acylic rubber, or combinations thereof; and

a plurality of glassy or semi-crystalline polymeric grafts comprising polystyrene, poly(α-methylstyrene) or another glassy styrenic polymer, polymethylmethacrylate or another glassy acrylic polymer, or combinations thereof, and

wherein each of the plurality of glassy or semi-crystalline polymeric grafts is attached to the rubbery polymeric backbone at one of the plurality of randomly spaced branch points; and wherein the random multigraft copolymer has a weight average molecular weight of about 400,000 or more, a volume fraction of glassy polymeric graft between about 14% and about 26%, and a strain at break of 1300% or greater; and

a tackifier.

17. The adhesive of claim 16, wherein the random multigraft copolymer comprises an architecture selected from a trifunctional comb architecture, a tetrafunctional centipede architecture, or a hexafunctional barbwire architecture.

18. The adhesive of claim 16, wherein the adhesive is a pressure sensitive adhesive or a hot melt adhesive.

19. The adhesive of claim 16, wherein the tackifier comprises rosins and derivatives thereof, terpenes, modified terpenes, an aliphatic resin, a cycloaliphatic resin, an aromatic resin, a hydrogenated hydrocarbon resin, a terpene-phenol resin, or mixtures thereof.

20. The adhesive of claim 16, further comprising one or more additives selected from waxes, plasticizers, anti-oxidants, stabilizers, decorative agents, biocides, flame retardants, anti-static agents, or fillers.

21. The adhesive of claim 20, wherein the decorative agent is a pigment, a dye or glitter.

22. A coated object comprising a coating layer wherein the coating layer comprises the random multigraft copolymer of claim 1, wherein the coating layer covers at least a portion of a surface of a wood, ceramic, glass, carbon fiber, metal, metallic, leather, fabric, stone, or plastic object.

23. The coated object of claim 22, wherein the object comprises an article of clothing, an eating/cooking utensil, a medical implant, a medical/surgical tool, or an electronic device.

24. The coated object of claim 22, wherein the object comprises a medical implant or a medical/surgical tool and wherein the coating layer further comprises a therapeutic agent additive selected from the group consisting of a carcinostatic, an immunosuppressive, an antibiotic, an antirheumatic, an antithrombotic, an antihyperlipidemic, an ACE inhibitor, a calcium antagonist, an integrin inhibitor, an antiallergic, an antioxidant, a GPIIb/IIIa antagonist, a retinoid, a flavonoid, a carotenoid, a lipid improving agent, a DNA synthesis inhibitor, a tyrosine kinase

inhibitor, an antiplatelet, a vascular smooth muscle antiproliferative agent, an antiinflammatory agent, an interferon, and a NO production accelerator.

25. The coated object of claim 22, wherein the coated object comprises a stent, wherein the stent comprises a metal or metallic wire mesh or a metal or metallic coil having a cylindrical shape, wherein the wire mesh or coil is covered by the coating layer.

26. A thermoplastic elastomer composition comprising:

a random multigraft copolymer comprising:

a rubbery polymeric backbone comprising a plurality of randomly spaced branch points; and

a plurality of glassy or semi-crystalline polymeric grafts, wherein each of the plurality of glassy or semi-crystalline polymeric grafts is attached to the rubbery polymeric backbone at one of the plurality of randomly spaced branch points; and wherein the random multigraft copolymer has a weight average molecular weight of about 400,000 or more, a volume fraction of glassy polymeric graft between about 14% and about 26%, and a strain at break of 1300% or greater.

27. The thermoplastic elastomer composition of claim 26, wherein the rubbery polymeric backbone has a glass transition temperature of about -40°C or less.

28. The thermoplastic elastomer composition of claim 26, comprising an average of three, four, five, six, seven, eight, or nine branch points.