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(54) **METHODS OF MAKING ORTHODONTIC APPLIANCES**

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***B29C 59/00*** (2006.01)

(52) **U.S. Cl.** ..... **264/129**; 264/16; 433/18

(58) **Field of Classification Search** ..... 264/129, 264/16; 433/18

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,372,796 A 12/1994 Wellinghoff
5,405,921 A 4/1995 Muschiatti et al.
5,670,583 A 9/1997 Wellinghoff
5,975,893 A 11/1999 Chishti et al.

FOREIGN PATENT DOCUMENTS

WO WO 00/32131 6/2000
WO WO 03/003935 1/2003
WO WO 03/094256 11/2003

OTHER PUBLICATIONS

International Search Report and Written Opinion of the International Searching Authority corresponding to PCT/US2005/027666, mailed Dec. 6, 2005.

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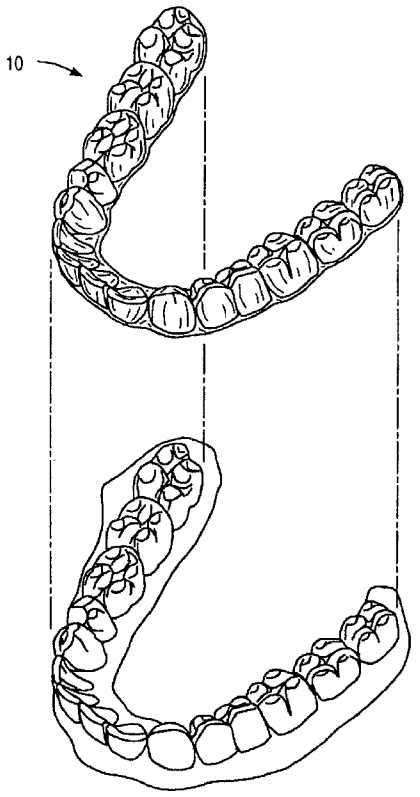
(57) **ABSTRACT**

Methods of making a removable dental positioning appliance include forming a sheet of transparent crystalline polymeric material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation. The polymeric material may then be annealed at a temperature above its glass transition temperature or cured if a curable material to enhance characteristics of the polymeric material. The polymeric material may be coated with a second transparent material.

**39 Claims, 2 Drawing Sheets**

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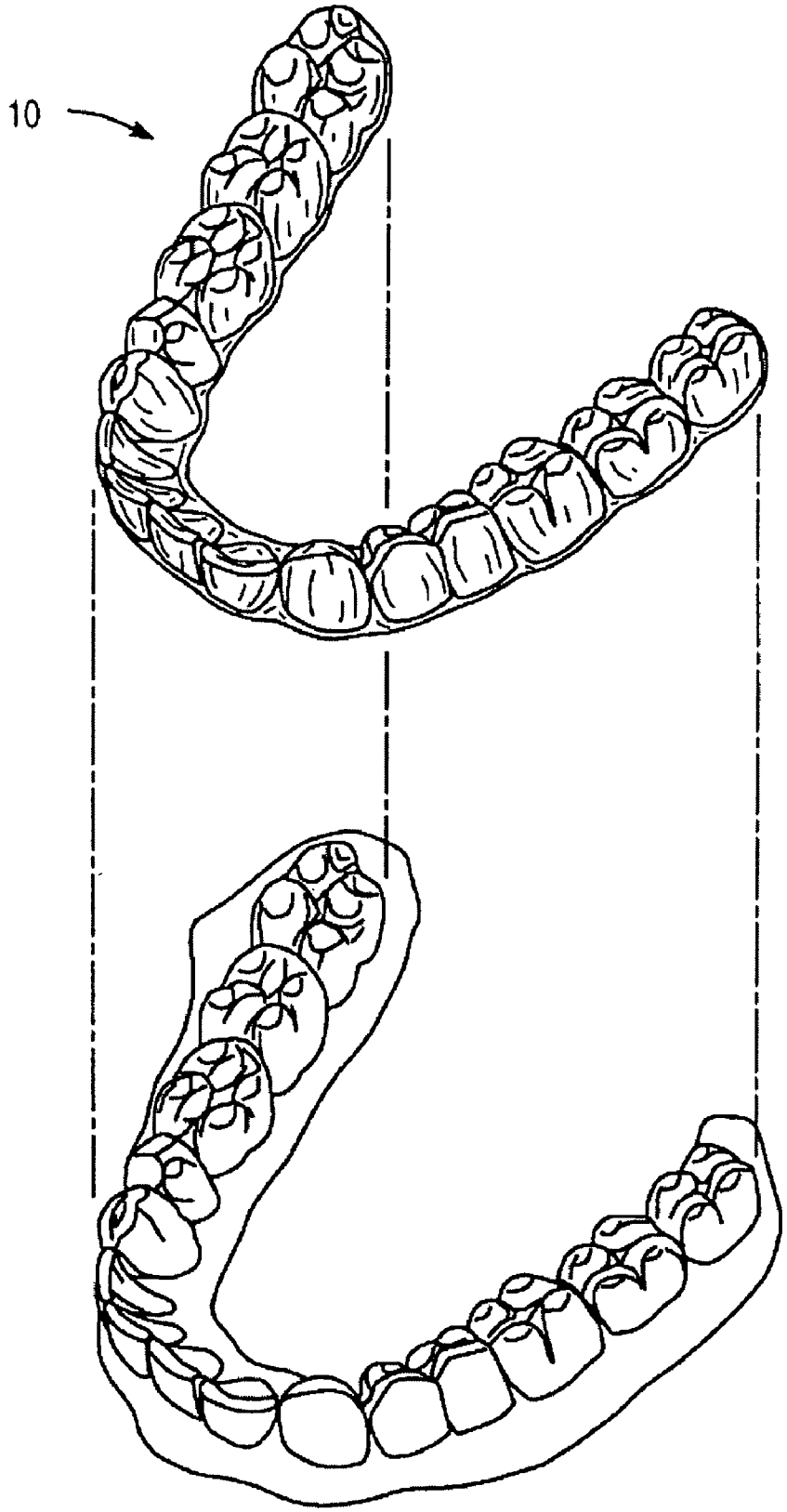


Fig. 1

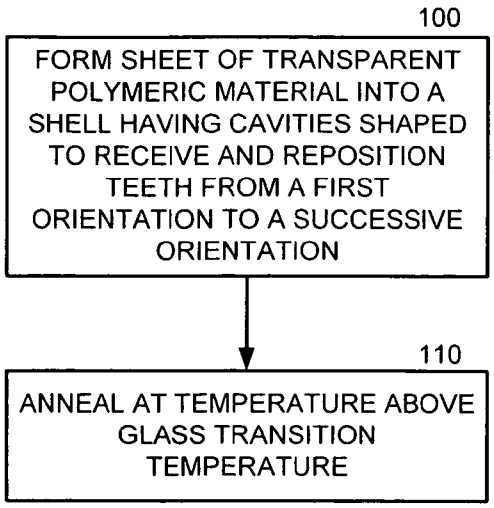


Fig. 2

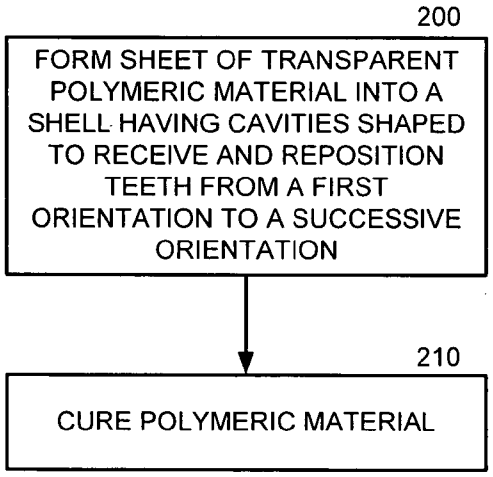


Fig. 3

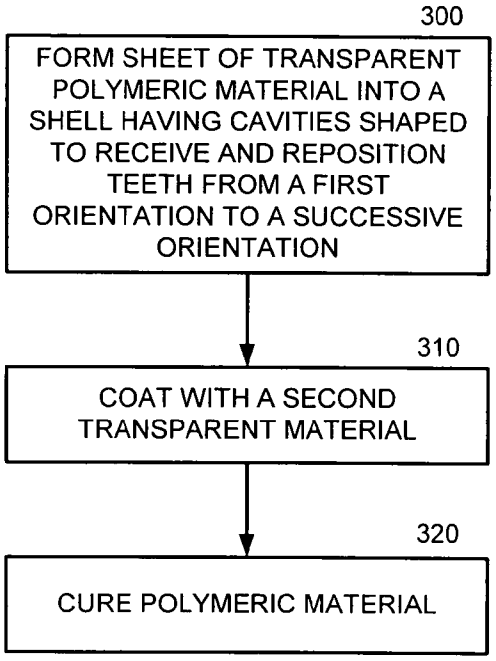


Fig. 4

# METHODS OF MAKING ORTHODONTIC APPLIANCES

## FIELD OF THE INVENTION

The present invention relates generally to orthodontics and, more particularly, to orthodontic appliances for incrementally moving teeth from an initial tooth arrangement to a final tooth arrangement.

## BACKGROUND OF THE INVENTION

Orthodontic treatments involve repositioning misaligned teeth and improving bite configurations for improved cosmetic appearance and dental function. Repositioning teeth is accomplished by applying controlled forces to the teeth over an extended period of time. This is conventionally accomplished by wearing what are commonly referred to as "braces." Braces include a variety of appliances such as brackets, bands, archwires, ligatures, and O-rings. After braces are bonded to the teeth, periodic meetings with an orthodontist are typically required to adjust the braces. This may involve installing different archwires with different force-inducing properties and/or may include replacing or tightening existing ligatures. Between meetings, the patient may be required to wear supplementary appliances, such as elastic bands or headgear, to supply additional or extraoral forces.

Although conventional braces can be effective, their use often is a tedious and time consuming process that requires many visits to an orthodontist. Moreover, from a patient's perspective, braces are unsightly and uncomfortable. Consequently, alternative orthodontic treatments have developed. A particularly promising approach relies on the use of elastic positioning appliances for realigning teeth. Such appliances comprise a thin shell of elastic material that generally conforms to a patient's teeth, but that is slightly out of alignment with the patient's initial tooth configuration. Placement of the elastic positioner over the teeth applies controlled forces in specific locations to gradually move the teeth into the new configuration. Repetition of this process with successive appliances having different configurations eventually moves a patient's teeth through a series of intermediate configurations to a final desired configuration. A full description of exemplary elastic polymeric positioning appliances and methods of using same are described in U.S. Pat. No. 5,975,893, commonly assigned to the assignee of the instant invention and which is incorporated herein by reference in its entirety.

Polymeric positioning appliances, such as those described in the '893 patent, are advantageous over conventional braces in that they are easy to use and they are generally transparent, providing an improved cosmetic appearance. Unfortunately, polymeric materials currently utilized in the production of these positioning appliances may undergo stress relaxation and creep, which can seriously degrade the ability of an appliance to reposition teeth as desired. In addition, polymeric materials currently utilized may be susceptible to degradation as a result of exposure to saliva and other chemicals present within a patient's mouth.

## SUMMARY OF THE INVENTION

According to embodiments of the present invention, a method of making a removable dental positioning appliance includes forming a sheet of transparent crystalline polymeric material into a shell having cavities shaped to receive and



reposition teeth from a first orientation to a successive orientation and then annealing the shell at a temperature above the glass transition temperature of the transparent crystalline polymeric material. Annealing is performed at a temperature and time sufficient to cause the annealed transparent crystalline polymeric material to preferably have a tensile strength at yield of greater than 6,000 psi, preferably have an elongation at yield of greater than 4%, preferably have an elongation at break of greater than 80%, preferably have a tensile modulus greater than 200,000 psi, preferably have a flexural modulus greater than 200,000 psi, preferably have stress relaxation over time of not more than 50%, and preferably have a transmissivity of light between 400 nm and 800 nm greater than 75%.

According to embodiments of the present invention, a method of making a removable dental positioning appliance includes forming a sheet of transparent curable polymeric material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation and then curing the polymeric material. When cured, the transparent polymeric material preferably has a tensile strength at yield of greater than 6,000 psi, preferably has an elongation at yield of greater than 4%, preferably has an elongation at break of greater than 80%, preferably has a tensile modulus greater than 200,000 psi, preferably has a flexural modulus greater than 200,000 psi, preferably has stress relaxation over time of not more than 50%, and preferably has a transmissivity of light between 400 nm and 800 nm greater than 75%. Even more preferably, the cured transparent polymeric material has a tensile strength at yield of greater than 8,800 psi, preferably has an elongation at yield of greater than 5%, preferably has an elongation at break of greater than 100%, preferably has a tensile modulus greater than 300,000 psi, preferably has a flexural modulus greater than 330,000 psi, preferably has stress relaxation over time of not more than 30%, and preferably has a transmissivity of light between 400 nm and 800 nm greater than 80%.

According to embodiments of the present invention, a method of making a removable dental positioning appliance includes forming a sheet of transparent curable polymeric material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation and then coating the polymeric shell with a second transparent material. If the coating is a curable material, the shell and coating are then subjected to curing operations to cure the coating material. The coated appliance preferably has a tensile strength at yield of greater than 6,000 psi, preferably has an elongation at yield of greater than 4%, preferably has an elongation at break of greater than 80%, preferably has a tensile modulus greater than 200,000 psi, preferably has a flexural modulus greater than 200,000 psi, preferably has stress relaxation over time of not more than 50%, and preferably has a transmissivity of light between 400 nm and 800 nm greater than 75%. Even more preferably, the coated appliance has a tensile strength at yield of greater than 8,800 psi, preferably has an elongation at yield of greater than 5%, preferably has an elongation at break of greater than 100%, preferably has a tensile modulus greater than 300,000 psi, preferably has a flexural modulus greater than 330,000 psi, preferably has stress relaxation over time of not more than 30%, and preferably has a transmissivity of light between 400 nm and 800 nm greater than 80%.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a perspective view of a removable dental positioning appliance that may be formed by various methods in accordance with embodiments of the present invention.

FIGS. **2**-**4** are flow charts illustrating methods of making a removable dental positioning appliance according to embodiments of the present invention

## DETAILED DESCRIPTION OF THE INVENTION

The present invention now is described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. The terminology used in the description of the invention herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used in the description of the invention and the appended claims, the singular forms "a", "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

U.S. Pat. No. 5,975,893 describes methods and systems for repositioning a patient's teeth from an initial tooth arrangement to a final tooth arrangement by placing a series of polymeric shell appliances in the patient's mouth. The appliances are not affixed to the patient's teeth and the patient may place and replace the appliances at any time during the procedure. The first appliance of the series has a geometry selected to reposition the teeth from the initial tooth arrangement to a first intermediate arrangement. After the first intermediate arrangement is approached or achieved, one or more additional (intermediate) appliances are successively placed on the teeth, where such additional appliances have geometries selected to progressively reposition teeth from the first intermediate arrangement through successive intermediate arrangement(s). The treatment is finished by placing a final appliance in the patient's mouth, where the final appliance has a geometry selected to progressively reposition teeth from the last intermediate arrangement to the final tooth arrangement. FIG. **1** illustrates an exemplary dental positioning appliance **10** described in the '893 patent.

The polymeric shells of dental positioning appliances for a patient, such as illustrated in FIG. **1**, are produced by initially obtaining a digital data set (IDDS) representing an initial tooth arrangement. The IDDS may be obtained in a variety of ways. For example, the patient's teeth may be scanned or imaged using well known technology, such as X-rays, three-dimensional x-rays, computer-aided tomographic images or data sets, magnetic resonance images, etc. The IDDS is then digitally manipulated via a computer to produce a final tooth arrangement, which is incorporated into a final digital data set (FDDS). Based on both the IDDS and the FDDS, a plurality of intermediate digital data sets (INTDDS's) are generated to correspond to successive intermediate tooth arrangements that correspond to tooth movement from the initial tooth arrangement to the final tooth arrangement.

Using the intermediate and final data sets, positive tooth models of a patient's teeth corresponding to each of the intermediate and final data sets are produced. After the positive models are prepared, a conventional pressure or vacuum molding machine may be used to produce the polymer shells of dental positioning appliances from a thermoformable material. The molding machine produces each of the appliances directly from a positive tooth model. The appliances are marked in some manner, typically by sequential numbering directly on the appliances or on tags, pouches, or other items which are affixed to or which enclose each appliance, to indicate their order of use.

According to embodiments of the present invention, methods of making removable dental positioning appliances, such as illustrated in FIG. **1**, with improved material properties are provided. Referring initially to FIG. **2**, a method of making a removable dental positioning appliance according to an embodiment of the present invention includes forming a sheet of transparent crystalline polymeric material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation (Block **100**) and then annealing the shell at a temperature above the glass transition temperature of the transparent crystalline polymeric material (Block **110**). Annealing is performed at a temperature and time sufficient to cause the annealed transparent crystalline polymeric material to preferably have a tensile strength at yield of greater than 6,000 psi, preferably have an elongation at yield of greater than 4%, preferably have an elongation at break of greater than 80%, preferably have a tensile modulus greater than 200,000 psi, preferably have a flexural modulus greater than 200,000 psi, preferably have stress relaxation over time of not more than 50%, and preferably have a transmissivity of light between 400 nm and 800 nm greater than 75%.

Even more preferably, annealing is performed at a temperature and time sufficient to cause the annealed transparent crystalline polymeric material to preferably have a tensile strength at yield of greater than 8,800 psi, preferably have an elongation at yield of greater than 5%, preferably have an elongation at break of greater than 100%, preferably have a tensile modulus greater than 300,000 psi, preferably have a flexural modulus greater than 330,000 psi, preferably have stress relaxation over time of not more than 30%, and preferably have a transmissivity of light between 400 nm and 800 nm greater than 80%.

Preferably, the annealing temperature is between the glass transition temperature and melting temperature of the transparent crystalline polymeric material (i.e., $T_g<T_{anneal}<T_m$). However, various annealing temperatures may be utilized. Annealing is preferably performed for at least about one minute. However, annealing may be performed for various time periods in accordance with embodiments of the present invention. Annealing times and temperatures will vary depending on the material of the shell and the coating material, as would be understood by those skilled in the art.

According to embodiments of the present invention, annealing may be performed in the presence of a nucleating agent disposed on or within the transparent crystalline polymeric material. As known to those skilled in the art, nucleating agents are chemical substances which, when incorporated in polymer materials, form nuclei for the growth of crystals in the polymer melt. For example, in certain polymers, a higher degree of crystallinity and more uniform crystalline structure may be obtained by adding a nucleating agent.

According to embodiments of the present invention, annealing may be performed selectively. The term "selective annealing" is used herein to indicate that a physical property

of the transparent crystalline polymeric material can be accurately controlled and modified to specific parameters via annealing. Selective annealing can allow for customization of a removable dental appliance. For example, crystallinity can be selectively increased, which can decrease the optical transparency, in portions of the shell of a removable dental appliance that are not visible when worn by a user. Other, visible portions may have less crystallinity and, thereby, more transparency. Selective annealing can occur by heating only certain portions of the shell. Other properties of the transparent crystalline polymeric material which may be controlled via selective annealing include, but are not limited to, tensile strength at yield, elongation at yield, elongation at break, tensile modulus, flexural modulus, stress relaxation, etc.

Annealing polymeric materials can also lead to densification of the amorphous phase, which is often referred to as physical aging. Such densification of amorphous phases can lead to an increase in modulus of the device.

Annealing may be performed by only heating selected portions of the shell of a removable dental positioning appliance. For example, a light source or laser may be utilized to heat selected portions of the shell of a removable dental positioning appliance. According to other embodiments of the present invention, annealing may be performed by adding chemical crosslink agents only to certain areas of the transparent crystalline polymeric material of the shell of a removable dental positioning appliance.

According to other embodiments of the present invention, annealing may be performed by selectively subjecting the transparent crystalline polymeric material to irradiation, such as e-beam irradiation, UV-visible irradiation and/or gamma irradiation.

According to embodiments of the present invention, exemplary transparent crystalline polymeric materials include, but are not limited to, liquid crystalline polymeric materials, styrenics, and ion-containing polymers. Applicants have discovered that removable dental positioning appliances formed from liquid crystalline polymers, styrenics, and ion-containing polymers that are annealed to have one or more of the above-listed characteristics are less susceptible to stress relaxation and creep than conventional dental positioning appliances. Moreover, Applicants have discovered that removable dental positioning appliances formed from liquid crystalline polymers, styrenics, and ion-containing polymers that are annealed to have one or more of the above-listed characteristics are less susceptible to degradation caused by exposure to saliva and other chemicals in a patient's mouth. Annealing significantly reduces internal stress levels, which increases chemical resistance of the material.

Exemplary liquid crystalline polymeric materials according to embodiments of the present invention include, but are not limited to branched liquid crystalline polymers and polyarylates. Crystallizable polyester compositions are also suitable and are described in U.S. Pat. No. 5,405,921, which is incorporated herein by reference in its entirety. Crystallizable polyesters utilized in accordance with embodiments of the present invention preferably have a glass transition temperature of at least 50° C. and/or a melting point of at least 150° C. In terms of intrinsic viscosity (IV), crystallizable polyesters should have an IV of at least about 0.5 as measured in a 1:1 by weight solution of methylene chloride and trifluoroacetic acid. The polyester base resin preferably is present in an amount of about 79-99 wt % based upon the total weight of the formulations used in the practice of this invention. A single polyester material need not be used. Copolyesters and blends may be used.

To obtain a clear product based upon crystallized polyester, the polymer must be oriented prior to the onset of crystallization. The orientation of the polyester results in the formation of elongated crystallites. Elongated crystallites allow incident light to pass without substantial diffraction, which results in a clear, transparent product.

Other exemplary crystalline polymeric materials that may be utilized in accordance with embodiments of the present invention include polyethylene terephthalate (PET) (e.g., DuPont Teijin Films MELINEX® brand polyester films and polyethylene naphthalate (PEN) films (e.g., DuPont Teijin Films TEONEX® brand polyethylene naphthalate (PEN) films. PET and PEN films have an inherent advantage over amorphous polymer films because PET and PEN are both semi-crystalline and biaxially oriented polymers. Moreover, PET and PEN films will typically absorb approximately 1,400 ppm of moisture at equilibrium.

According to other embodiments of the present invention, dental positioning appliances may be formed from PVC modified with ELVALOY® brand ketone ethylene ester (DuPont, Wilmington, Del.). ELVALOY® brand modified PVC has been found to be more resistant to creep than PVC and HDPE.

Exemplary styrenic polymeric materials according to embodiments of the present invention include, but are not limited to polystyrene (PS), expanded polystyrene (EPS), acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN), styrene block copolymers (SBC), unsaturated polyester resins (uPES), styrene butadiene rubber (SBR), and styrene butadiene latex (SBL). Styrenic polymeric materials are rigid, transparent, tough, resistant to grease, stress cracking and crazing. Styrenic polymeric materials are also easily processed and resistant to food stains. Styrenic polymeric materials are available from a variety of sources including Bayer AG, Leverkusen, Germany, The Dow Chemical Company, Midland, Mich., and PolyOne Corporation, Avon Lake, Ohio.

Exemplary ion-containing polymeric materials include, but are not limited to, SURLYN® brand ionomer resin (DuPont, Inc., Wilmington, Del.). Other important commercial ionomers include NAFION® brand ionomer polymers (Ion Power, Inc., Bear, Del.). NAFION® brand ionomer polymers are sulfonated tetrafluorethylene ionomer and sulfonated polystyrene. Ionomers have significantly better properties than the un-ionized precursor because the ionic groups phase separate into ion-rich domains.

Other exemplary polymeric materials that can be formed and annealed, in accordance with embodiments of the present invention, include transparent polymeric materials with high glass transition temperatures (e.g., at least 155° C.). Exemplary transparent polymeric materials having high glass transition temperatures include, but are not limited to norbornene-containing polymers, metallocene, metal-catalyzed polyolefins, cyclo-olefins, poly(methyl-1-pentene), amorphous aromatic resins, poly(benzophenone)s, polyamides, thermoplastic polyurethanes, polyetherimides, poly(arylene ether ketone)s, polysulfones, biphenyl endcapped poly (acrylene ether) polymers, polycarbonates, polyesters, poly (estercarbonate)s, cellulosics, and acrylics.

Other exemplary transparent materials having high glass transition temperatures include PARAMAX™ brand self-reinforcing thermoplastic (Mississippi Polymer Technologies) and polyamides. PARAMAX™ brand self-reinforcing thermoplastic is a very hard polymer with a low coefficient of thermal expansion, and a high refractive index. PARAMAX™ brand self-reinforcing thermoplastic can be molded extruded and cast from solution and produces clear alloys

with other engineering thermoplastics. PARAMAX™ brand self-reinforcing thermoplastic is miscible with polycarbonate and polysulfone. PARAMAX™ brand self-reinforcing thermoplastic has a high surface hardness which provides excellent scratch resistance. Other exemplary transparent materials having high glass transition temperatures include SUNTUF® brand polycarbonate, PALSUN® brand polycarbonate and PALTUF™ brand polycarbonate sheets, PALGLAS® brand acrylic sheets; PAL-G™ brand co-polyester sheets, and PAL-RUF® brand PVC sheets, all available from Suntuf, Inc. Kutztown, Pa.

According to embodiments of the present invention, transparent acrylic and polycarbonate materials having high glass transition temperatures are processed with a supermicrocellular foaming technique developed by Wright Materials Research Co., Beavercreek, Ohio. This technique utilizes biphenyl endcapped poly(acrylene ether) polymers.

Other exemplary transparent materials having high glass transition temperatures include TROGAMID® brand transparent polyamides (Degussa AG, Marl, Germany). TROGAMID® brand transparent polyamides are permanently transparent, have high chemical resistance, and have a low tendency to creep.

Other exemplary materials that can be formed and annealed, in accordance with embodiments of the present invention, include laminates and/or blends of transparent polymeric materials. Exemplary blends of transparent polymers include, but are not limited to, polyester blends such as polybutylene terephthalate (PBT) blends and polyethylene terephthalate (PET) blends. Polyester blends, in general, have high strength and rigidity. Exemplary transparent laminates include, but are not limited to, polycarbonate-based laminates, acrylic-based laminates, PARAMAX™ brand self-reinforcing thermoplastic polymers, polycarbonates, and polysulfone.

Referring to FIG. **3**, a method of making a removable dental positioning appliance according to an embodiment of the present invention includes forming a sheet of transparent curable polymeric material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation (Block **200**) and then curing the polymeric material (Block **210**). When cured, the transparent polymeric material preferably has a tensile strength at yield of greater than 6,000 psi, preferably has an elongation at yield of greater than 4%, preferably has an elongation at break of greater than 80%, preferably has a tensile modulus greater than 200,000 psi, preferably has a flexural modulus greater than 200,000 psi, preferably has stress relaxation over time of not more than 50%, and preferably has a transmissivity of light between 400 nm and 800 nm greater than 75%. Even more preferably, the cured transparent polymeric material preferably has a tensile strength at yield of greater than 8,800 psi, preferably has an elongation at yield of greater than 5%, preferably has an elongation at break of greater than 100%, preferably has a tensile modulus greater than 300,000 psi, preferably has a flexural modulus greater than 330,000 psi, preferably has stress relaxation over time of not more than 30%, and preferably has a transmissivity of light between 400 nm and 800 nm greater than 80%.

Exemplary curable transparent polymeric materials that may be utilized in accordance with embodiments of the present invention include, but are not limited to, epoxies, sol-gel coatings, polyurethanes, polyureas, and unsaturated polyesters.

According to embodiments of the present invention, curing the transparent polymeric material may be performed by irradiating the transparent polymeric material with ionizing electromagnetic radiation such as gamma radiation, ultraviolet radiation, microwave radiation, electron beam radiation, x-ray radiation, etc. To facilitate curing with ionizing electromagnetic radiation, the transparent polymeric material may contain various additives including, but not limited to, radiation stabilizers and antioxidants which act to protect the polymeric material from damage caused by the radiation. Such additives are referred to as "antirads" and function either as reactants, combining readily with radiation-generated free radicals in the polymer material, or as energy absorbers, preventing the radiation from interacting with the polymer itself.

In addition to curing, ionizing radiation may be utilized to enhance the material characteristics of polymers used in dental positioning appliances in accordance with embodiments of the present invention. Many important physical and chemical properties of polymers can be modified with ionizing radiation including, but not limited to, molecular weight, polymer chain length, entanglement, polydispersity, branching, pendant functionality, and chain termination. Radiation, such as gamma and electron beam irradiation, may also be utilized to sterilize the polymeric material of dental positioning appliances, according to embodiments of the present invention.

Embodiments of the present invention are not limited to curing with ionizing electromagnetic radiation. Curing may also be performed via the addition of heat (i.e., thermal curing), as would be understood by those skilled in the art.

Applicants have discovered that removable dental positioning appliances coated with materials as described above are less susceptible to stress relaxation and creep than conventional dental positioning appliances. Moreover, Applicants have discovered that removable dental positioning appliances coated with materials as described above are less susceptible to degradation caused by exposure to saliva and other chemicals in a patient's mouth.

Referring to FIG. **4**, a method of making a removable dental positioning appliance according to an embodiment of the present invention includes forming a sheet of transparent curable polymeric material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation (Block **300**) and then coating the polymeric shell with a second transparent material (Block **310**). If the coating is a curable material, the shell and coating are then subjected to curing operations (Block **320**) to cure the coating material. According to embodiments of the present invention, curing operations may be performed by irradiating the transparent polymeric material with ionizing electromagnetic radiation such as gamma radiation, ultraviolet radiation, microwave radiation, electron beam radiation and x-ray radiation. To facilitate curing with ionizing electromagnetic radiation, the transparent polymeric material may contain various additives including, but not limited to, radiation stabilizers and antioxidants. Embodiments of the present invention are not limited to curing with ionizing electromagnetic radiation. Curing may also be performed via the addition of heat (i.e., thermal curing), as would be understood by those skilled in the art.

A coated polymeric shell of a removable dental positioning appliance, according to embodiments of the present invention, preferably has a tensile strength at yield of greater than 6,000 psi, preferably has an elongation at yield of greater than 4%, preferably has an elongation at break of greater than 80%, preferably has a tensile modulus greater than 200,000 psi, preferably has a flexural modulus greater than 200,000 psi, preferably has stress relaxation over time of not more than 50%, and preferably has a transmissivity of light between 400

nm and 800 nm greater than 75%. Even more preferably, the coated polymeric shell has a tensile strength at yield of greater than 8,800 psi, preferably has an elongation at yield of greater than 5%, preferably has an elongation at break of greater than 100%, preferably has a tensile modulus greater than 300,000 psi, preferably has a flexural modulus greater than 330,000 psi, preferably has stress relaxation over time of not more than 30%, and preferably has a transmissivity of light between 400 nm and 800 nm greater than 80%.

According to embodiments of the present invention, the first transparent material used to form the shell may include polyurethanes, liquid crystalline polymeric materials, styrenics, ion-containing polymers, polymeric laminates and polymeric blends. Exemplary liquid crystalline polymeric materials include, but are not limited to, polyesters, polyamides, polycarbonates, polyolefins, poly(cycloolefins), branched liquid crystalline polymers and polyarylates.

Exemplary styrenic polymeric materials according to embodiments of the present invention include, but are not limited to polystyrene (PS), expanded polystyrene (EPS), acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN), styrene block copolymers (SBC), unsaturated polyester resins (uPES), styrene butadiene rubber (SBR), and styrene butadiene latex (SBL). Exemplary ion-containing polymeric materials include, but are not limited to, SURLYN® brand resin and NAFION® brand polymers.

According to embodiments of the present invention, the first transparent material used to form the shell may have a glass transition temperature of at least 100° C.

According to embodiments of the present invention, the first transparent material used to form the shell may include filler material including, but not limited to, inorganic materials and/or organic materials. Exemplary inorganic filler materials include, but are not limited to, metal oxides, oxygenates, carbonates, halides, and sulfates. Exemplary organic filler materials include, but are not limited to, waxes and oligomeric polymers.

According to embodiments of the present invention, the first transparent material used to form the shell may include ultra-high molecular weight polymers.

According to embodiments of the present invention, the first transparent material used to form the shell may include uniaxially oriented polymers and/or bi-axially oriented polymer.

According to embodiments of the present invention, the first transparent material used to form the shell may include BARIX™ brand vapor barrier film, available from Vitex Systems, San Jose, Calif.

According to embodiments of the present invention, the second transparent material may be a curable polymeric material. Exemplary curable coating materials, according to embodiments of the present invention, include, but are not limited to, epoxies, acrylics, alkyds, acrylate resins which incorporate corrosion protective fillers and other materials, multifunctional acrylates (MFMs), acrylated oligomers, or monofunctional diluent monomers, solvent free powder coatings, sol-gel coatings, polyurethanes, polyureas, and unsaturated polyesters. Various photoinitiators may be utilized including, but not limited to, free radical, acid, cationic, etc. Curing the second transparent material may include irradiating the coating with ionizing electromagnetic radiation, such as gamma radiation, ultraviolet radiation, microwave radiation, electron beam radiation, x-ray radiation, etc. The second transparent material may include radiation stabilizers and/or antioxidants.

According to embodiments of the present invention, the second transparent material may be durable, non-curable polymeric material. Exemplary non-curable polymeric materials include, but are not limited to, acrylics, silicone, inorganic-containing materials, polycarbonates, and polyurethanes.

According to embodiments of the present invention, the second transparent material has a glass transition temperature or a melting point of at least 150° C.

According to embodiments of the present invention, the second transparent material includes BARIX™ brand vapor barrier film.

According to embodiments of the present invention, the second transparent material includes advanced thermoplastic composite (ATC) material.

According to embodiments of the present invention, the second transparent material includes ISOPLAST® 2530 polyurethane resin (The Dow Chemical Company, Midland, Mich.). ISOPLAST® 2530 polyurethane resin is a clear amorphous polymer with excellent chemical resistance, high heat, low moisture sensitivity, toughness, and dimensional stability.

According to embodiments of the present invention, the second transparent material may contain a material, such as silicon dioxide, to improve abrasion resistance of the removable dental positioning appliance. According to embodiments of the present invention, the second transparent material may contain a material, such as silicon dioxide, that serves as a barrier to harmful substances (e.g., water vapor, oxygen, etc.). According to embodiments of the present invention, the second transparent material may contain a material that avoids the formation of fog. Exemplary antifog materials include, but are not limited to, silicon oxides.

In each of the above-described embodiments, the transparent polymeric material of the dental positioning appliance may include uniaxially oriented polymers and/or bi-axially oriented polymers.

In each of the above-described embodiments, the transparent polymeric material of the dental positioning appliance may include filler material including, but not limited to, inorganic materials and/or organic materials. Exemplary inorganic filler materials include, but are not limited to, metal oxides, oxygenates, carbonates, halides, and sulfates. U.S. Pat. Nos. 5,372,796 and 5,670,583, each of which is incorporated herein by reference in its entirety, describe metal oxide clusters and ceramers (polymer-ceramic composites). According to embodiments of the present invention, alloys of polymers with ceramic particles of diameter much smaller than the wavelength of visible light can be used to produce a material with a high refractive index, and that are scratch and corrosion resistant. Exemplary organic filler materials include, but are not limited to, waxes and oligomeric polymers.

In each of the above-described embodiments, the transparent polymeric material of the dental positioning appliance may include additives, such as ultra-high molecular weight polymers. An exemplary ultra-high molecular weight polymer that may be utilized in accordance with embodiments of the present invention is ultra-high molecular weight polyethylene (UHMWPE), available from Cambridge Polymer Group, Boston, Mass. The wear properties of ultra-high molecular weight polymers, as well as other types of polymers, can be enhanced with radiation, such as electron beam and gamma irradiation.

That which is claimed is:

**1**. A method of making a removable dental positioning appliance, comprising:

forming a sheet of a first transparent material into a shell having cavities shaped to receive and reposition teeth

from a first orientation to a successive orientation, wherein the first transparent material is selected from the group consisting of styrenics, ion-containing polymers, polymeric laminates thereof and polymeric blends thereof; and

applying a coating of a second transparent material onto the shell such that the shell has a tensile strength at yield of greater than 6,000 psi, an elongation at yield of greater than 4%, an elongation at break of greater than 80%, a tensile modulus greater than 200,000 psi, a flexural modulus greater than 200,000 psi, stress relaxation over time of not more than 50%, and a transmissivity of light between 400 nm and 800 nm greater than 75%.

**2**. The method of claim **1**, wherein the first transparent material has a glass transition temperature Tg of at least 100° C.

**3**. The method of claim **1**, wherein the second transparent material comprises a curable polymeric material.

**4**. The method of claim **3**, wherein the curable polymeric material is selected from the group consisting of epoxies, acrylics, alkyds, acrylate resins which incorporate corrosion protective fillers and other materials, multifunctional acrylates (MFMs), acrylated oligomers, or monofunctional diluent monomers, solvent free powder coatings, sol-gel coatings, polyurethanes, polyureas, and unsaturated polyesters.

**5**. The method of claim **3**, further comprising curing the second transparent material.

**6**. The method of claim **5**, wherein curing the second transparent material comprises irradiating the coating with ionizing electromagnetic radiation selected from the group consisting of gamma radiation, ultraviolet radiation, microwave radiation, electron beam radiation and x-ray radiation.

**7**. The method of claim **6**, wherein the second transparent material comprises radiation stabilizers.

**8**. The method of claim **6**, wherein the second transparent material comprises antioxidants.

**9**. The method of claim **1**, wherein the second transparent material comprises a durable, non-curable polymeric material.

**10**. The method of claim **9**, wherein the non-curable, durable polymeric material is selected from the group consisting of acrylics, silicone, inorganic-containing materials, polycarbonates, and polyurethanes.

**11**. The method of claim **1**, wherein the second transparent material has a glass transition temperature or a melting point of at least 150° C.

**12**. The method of claim **1**, wherein the first transparent material comprises uniaxially oriented polymers.

**13**. The method of claim **1**, wherein the first transparent material comprises bi-axially oriented polymers.

**14**. The method of claim **1**, wherein at least one of the first and second transparent materials comprises filler material selected from the group consisting of inorganic materials and organic materials.

**15**. The method of claim **1**, wherein at least one of the first and second transparent materials comprises inorganic filler material selected from the group consisting of metal oxides, oxygenates, carbonates, halides, and sulfates.

**16**. The method of claim **1**, wherein at least one of the first and second transparent materials comprises organic filler material selected from the group consisting of waxes and oligomeric polymers.

**17**. The method of claim **1**, wherein the first transparent material comprises ultra-high molecular weight polymers.

**18**. The method of claim **1**, wherein the first transparent material comprises ionomer resin.

**19**. The method of claim **1**, wherein at least one of the first and second transparent materials comprises a vapor barrier film.

**20**. The method of claim **1**, wherein the second transparent material comprises Sol-gel.

**21**. The method of claim **1**, wherein the second transparent material comprises advanced thermoplastic composite (ATC) material.

**22**. The method of claim **1**, wherein the sheet and the coating each have a respective different elastic modulus.

**23**. The method of claim **22**, wherein the coating has a higher elastic modulus than the sheet.

**24**. The method of claim **1**, wherein the first transparent polymeric material comprises styrenic polymeric material selected from the group consisting of acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN), and styrene block copolymers (SBC).

**25**. A method of making a removable dental positioning appliance, comprising:

forming a sheet of a first transparent material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation wherein the first transparent material is selected from the group consisting of styrenics, ion-containing polymers, polymeric laminates thereof and polymeric blends thereof; and

applying a coating of a second transparent material onto the shell, wherein the coating has a higher tensile and flexural modulus than the sheet, and wherein the shell has a tensile modulus greater than 200,000 psi, and a flexural modulus greater than 200,000 psi.

**26**. The method of claim **25**, wherein the shell has a tensile strength at yield of greater than 6,000 psi.

**27**. The method of claim **25**, wherein the shell has an elongation at yield of greater than 4%, and an elongation at break of greater than 80%.

**28**. The method of claim **25**, wherein the shell has a stress relaxation over time of not more than 50%.

**29**. The method of claim **25**, wherein the shell has a transmissivity of light between 400 nm and 800 nm greater than 75%.

**30**. A method of making a removable denial positioning appliance, comprising:

forming a sheet of a first transparent material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation, wherein the shell has a tensile strength at yield of greater than 4,000 psi; and

applying a coating of a second transparent material onto the shell, wherein the coating has a higher tensile and flexural modulus than the sheet, and wherein at least one of the first and second transparent materials comprises organic filler material selected from the group consisting of waxes and oligomeric polymers.

**31**. The method of claim **30**, wherein the shell has a tensile modulus greater than 200,000 psi, and a flexural modulus greater than 200,000 psi.

**32**. A method of making a removable dental positioning appliance, comprising:

forming a sheet of a first transparent material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation, wherein the first transparent material comprises material selected from the group consisting of styrenics, ion-containing polymers, polymeric laminates thereof, and polymeric blends thereof; and

applying a coating of a second transparent material onto the shell, wherein the coating has a higher tensile and flexural modulus than the sheet, and wherein the shell has a tensile modulus greater than 200,000 psi, and a flexural modulus greater than 200,000 psi.

**33**. A method of making a removable dental positioning appliance, comprising:

forming a sheet of a first transparent material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation;

applying a coating of a second transparent material onto the shell such that the shell has a tensile strength at yield of greater than 6,000 psi, an elongation at yield of greater than 4%, an elongation at break of greater than 80%, a tensile modulus greater than 200,000 psi, a flexural modulus greater than 200,000 psi, stress relaxation over time of not more than 50%, and a transmissivity of light between 400 nm and 80 nm greater than 75%, wherein the second transparent material comprises a curable polymeric material comprising antioxidants; and

curing the second transparent material by irradiating the coating with ionizing electromagnetic radiation selected from the group consisting of gamma radiation, ultraviolet radiation, microwave radiation, electron beam radiation and x-ray radiation.

**34**. A method of making a removable dental positioning appliance, comprising:

forming a sheet of a first transparent material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation; and

applying a coating of a second transparent material onto the shell such that the shell has a tensile strength at yield of greater than 6,000 psi, an elongation at yield of greater than 4%, an elongation at break of greater than 80%, a tensile modulus greater than 200,000 psi, a flexural modulus greater than 200,000 psi, stress relaxation over time of not more than 50%, and a transmissivity of light between 400 nm and 800 nm greater than 75%;

wherein at least one of the first and second transparent materials comprises filler material selected from the group consisting of inorganic materials and organic materials.

**35**. A method of making a removable dental positioning appliance, comprising:

forming a sheet of a first transparent material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation; and

applying a coating of a second transparent material onto the shell such that the shell has a tensile strength at yield of greater than 6,000 psi, an elongation at yield of greater than 4%, an elongation at break of greater than 80%, a tensile modulus greater than 200,000 psi, a flexural modulus greater than 200,000 psi, stress relaxation over time of not more than 50%, and a transmissivity of light between 400 nm and 800 nm greater than 75%;

wherein at least one of the first and second transparent materials comprises inorganic filler material selected from the group consisting of metal oxides, oxygenates, carbonates, halides, and sulfates.

**36**. A method of making a removable dental positioning appliance, comprising:

forming a sheet of a first transparent material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation; and

applying a coating of a second transparent material onto the shell such that the shell has a tensile strength at yield of greater than 6,000 psi, an elongation at yield of greater than 4%, an elongation at break of greater than 80%, a tensile modulus greater than 200,000 psi, a flexural modulus greater than 200,000 psi, stress relaxation over time of not more than 50%, and a transmissivity of light between 400 nm and 800 nm greater than 75%;

wherein at least one of the first and second transparent materials comprises organic filler material selected from the group consisting of waxes and oligomeric polymers.

**37**. A method of making a removable dental positioning appliance, comprising:

forming a sheet of a first transparent material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation, wherein the first transparent material comprises ultra-high molecular weight polymers; and

applying a coating of a second transparent material onto the shell such that the shell has a tensile strength at yield of greater than 6,000 psi, an elongation at yield of greater than 4%, an elongation at break of greater than 80%, a tensile modulus greater than 200,000 psi, a flexural modulus greater than 200,000 psi, stress relaxation over time of not more than 50%, and a transmissivity of light between 400 nm and 800 nm greater than 75%.

**38**. A method of making a removable dental positioning appliance, comprising:

forming a sheet of a first transparent material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation; and

applying a coating of a second transparent material onto the shell such that the shell has a tensile strength at yield of greater than 6,000 psi, an elongation at yield of greater than 4%, an elongation at break of greater than 80%, a tensile modulus greater than 200,000 psi, a flexural modulus greater than 200,000 psi, stress relaxation over time of not more than 50%, and a transmissivity of light between 400 nm and 800 nm greater than 75%, wherein the second transparent material comprises Sol-gel.

**39**. A method of making a removable dental positioning appliance, comprising:

forming a sheet of a first transparent material into a shell having cavities shaped to receive and reposition teeth from a first orientation to a successive orientation; and

applying a coating of a second transparent material onto the shell such that the shell has a tensile strength at yield of greater than 6,000 psi, an elongation at yield of greater than 4%, an elongation at break of greater than 80%, a tensile modulus greater than 200,000 psi, a flexural modulus greater than 200,000 psi, stress relaxation over time of not more than 50%, and a transmissivity of light between 400 nm and 800 nm greater than 75%, wherein the second transparent material comprises advanced thermoplastic composite (ATC) material.

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UNITED STATES PATENT AND TRADEMARK OFFICE

# CERTIFICATE OF CORRECTION



PATENT NO. : 7,641,828 B2
APPLICATION NO. : 10/963252
DATED : January 5, 2010
INVENTOR(S) : DeSimone et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In the Claims:

Column 13, Claim 33, Line 18: Please correct "80 nm" to read -- 800 nm --

Signed and Sealed this

Twenty-third Day of March, 2010

David J. Kappos

David J. Kappos
*Director of the United States Patent and Trademark Office*