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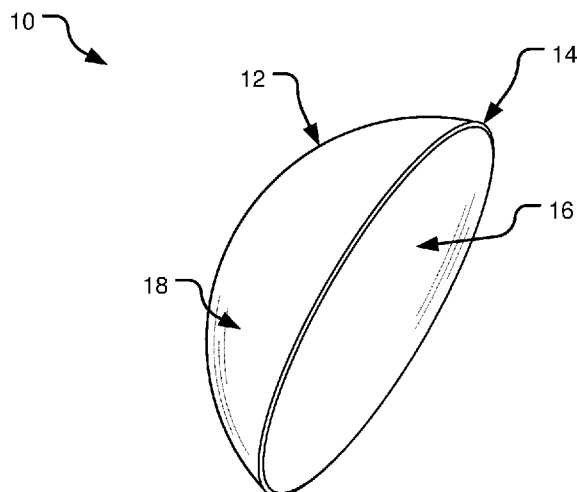


FIG. 1

(57) Abstract: Polymeric compositions comprising at least one urethane-based acrylate copolymer, the cured compositions particularly suited for lenses such as intraocular lenses and contact lenses, and other corneal prosthetics.



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COPOLYMER FORMULATION FOR LENSES

CROSS-REFERENCE

This PCT application claims priority to U.S. provisional application 62/103,997, filed January 15, 2015. For U.S. purposes, this application is a continuation application of U.S. provisional application 62/103,997, filed January 15, 2015.

TECHNICAL FIELD

The present invention generally relates to polymeric compositions for ophthalmic uses.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

None.

BACKGROUND

In a normally functioning eye, the cornea and crystalline lens of the eye work in unison to focus a clear image on the retina. The cornea provides the bulk of the focusing power and the lens provides the fine-tune focusing. The natural crystalline lens is flexible and changes shape, allowing the eye to focus. Due to aging, or as the result of an injury, the lens may need to be replaced. Surgically implantable lenses have been developed to replace the eye's natural crystalline lens with an artificial lens in attempts to return to the eye's vision to its natural state.

SUMMARY

The present disclosure is directed to polymeric compositions comprising at least one urethane-based acrylate copolymer, the cured compositions particularly suited for ophthalmic-use lenses such as intraocular lenses, contact lenses and other corneal prosthetics.

In some implementations, the composition comprises at least 60 wt-% of urethane-based acrylate copolymer.

In some implementations, the ratio of the urethane-based acrylate copolymer and any non-urethane based acrylate copolymer is no more than 3.5.

In one particular implementation, the urethane-based acrylate(s) is 67-72 wt-% of the total, uncured polymeric composition, with a ratio of the urethane-based acrylate copolymer and any non-urethane based acrylate copolymer no more than 3.5.

Urethane-based acrylate(s) are preferred for the polymer composition because they enable secondary interactions (reversible hydrogen bonding) within the composition. In some implementations, other monomer, polymer or copolymer material(s) may be used in place of the urethane-based acrylate(s), as long as they provide secondary interactions (reversible hydrogen bonding) in the composition and meet the criteria for an intraocular lens.

In some implementations, the polymeric composition may be used as a coating on a previously formed lens.

These and various other features and advantages will be apparent from a reading of the following detailed description.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a perspective view of a lens according to the present disclosure.

FIG. 2 is a photomicrograph of a polymeric composition showing no glistening.

FIG. 3 is a photomicrograph of a polymeric composition showing glistening.

FIG. 4 is a graphical representation of percent transmittance for various polymeric compositions.

DETAILED DESCRIPTION

The present disclosure describes various polymeric compositions particularly configured for intraocular lenses, such as implantable lenses and surface or removable lenses (e.g., contact lenses). The polymeric compositions include at least one urethane-based acrylic copolymer. The compositions, when cured to at least 98% conversion, provide lenses that are non-tacky, biocompatible, hydrophobic, have acceptable refractive index, and are free of visible imperfections and glistening.

Some intraocular lenses are ophthalmological implants or prostheses surgically implanted in the eye of patients suffering from various ailments, such as cataracts, to replace their failing crystalline lens. During this surgical procedure, the surgeon removes the natural

crystalline lens from the patient and replaces it with a synthetic (e.g., polymeric) intraocular lens. The intraocular lens is implanted in the patient's eye by an injector equipped with an injection tube. To ensure that the procedure causes as little trauma as possible for the patient, and to avoid the development of post-operative astigmatism, the incision made in the cornea must be as small as possible.

The intraocular lens, which has clearly larger diameter, must therefore be folded, curled or rolled in order to permit it to pass through this incision of very short length. The folded lens is placed in the charging chamber of an injection cartridge, which may curl the lens upon itself if it is not already curled or folded. Once the injection cartridge is mounted in the injector, a piston pushes the rear end of the lens into the injection tube of the injector, compressing it, and causing it to be expelled into the patient's eye. The intraocular lens must be deployed rapidly so that it can be positioned correctly and be capable of fulfilling its function of optical correction in satisfactory manner.

Once in the patient's eye, the intraocular lens must be capable of deploying completely on its own, without remaining stuck to itself, and in a relatively short time, so that it becomes positioned correctly in eye and recovers its optical characteristics.

To ensure that the lens can be placed without problems, the lens must be sufficiently flexible that it can be folded and curled up on itself, but sufficiently non-tacky to uncurl quickly. It must resist stretching and the pushing pressure without being ruptured and without breaking the injection tube. Additionally, it must have acceptable optical properties, such as refractive index, free of visible imperfections, and of course, be biocompatible.

In the following description, reference is made to the accompanying drawing that forms a part hereof and in which are shown by way of illustration at least one specific embodiment. The following description provides additional specific embodiments. It is to be understood that other embodiments are contemplated and may be made without departing from the scope or spirit of the present invention. The following detailed description, therefore, is not to be taken in a limiting sense. While the present invention is not so limited, an appreciation of various aspects of the invention will be gained through a discussion of the examples provided below.

As used herein, the singular forms "a", "an", and "the" encompass embodiments having plural referents, unless the content clearly dictates otherwise. As used in this specification and the appended claims, the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

Spatially related terms, including but not limited to, “lower”, “upper”, “beneath”, “below”, “above”, “on top”, etc., if used herein, are utilized for ease of description to describe spatial relationships of an element(s) to another. Such spatially related terms encompass different orientations of the device in addition to the particular orientations depicted in the figures and described herein. For example, if a structure depicted in the figures is turned over or flipped over, portions previously described as below or beneath other elements would then be above or over those other elements.

Turning to FIG. 1, a contact lens 10 is illustrated. Although a contact lens 10 is illustrated, the lens can be an implantable lens, such as an intraocular lens. Lens 10 has a flexible body 12 that naturally has a domed shape, a peripheral edge 14, and a first side 16 and a second side 18. In this illustrated embodiment, the first side 16 is the side that is closer to the cornea (for an implanted lens) or to the eye (for a contact lens) and has a concave shape, and second side 18 has a convex shape.

Lens 10 is non-tacky, biocompatible, has acceptable refractive index, and is free of visible imperfections and glistening. Lens 10 is sufficiently flexible and durable to survive multiple bending and unbending cycles while remaining undamaged.

Additionally, lens 10 is hydrophobic, which is unexpected and unobvious. It is well known that hydrophilic polymeric materials are more flexible (deformable) than hydrophobic materials, since the flexible of the material depends on the amount of water absorbed.

Hydrophilic materials are hard and compact in the absence of water, permitting them to be machined easily at room temperature. When they are hydrated, they dilate and become soft and flexible and non-tacky. Hydrophilic materials are optimal for intraocular lenses. However, Applicant found that hydrophobic lenses can exhibit numerous desirable properties. For example, hydrophobic lens have low equilibrium water content, making them biofriendly with less calcification and deposits, for example, protein deposits, which occur less with hydrophobic materials compared to hydrophilic materials.

Upon curing, for an ideal lens, the conversion of the polymer composition is 100%, shrinking is zero (0%), there is no tack to the cured material, there is zero (0%) extraction, the material is glistening free, and the equilibrium water content (EWC) is less than 4%.

A low tack or no tack material is desired so that the lens will not stick to the injector, injection tube and other device components and negatively impact unfolding. For an intraocular lens that is low tack, the haptic a will stick less to the optic, and for a contact lens that is low tack, the lens will open up more readily when folded. Low tack materials also facilitate injection through a smaller lumen with less torque/required force. Low tack

materials generally attract less dust and adhere less to surfaces during the manufacturing process, thus facilitating scale up of manufacturing.

As indicated above, a hydrophobic material is desired. In addition to hydrophobic lenses having low equilibrium water content making them biofriendly with less calcification and deposits, hydrophobic lenses have low shrinkage and high conversion rates in curing, which allow easier and more precise molding. A hydrophobic material has a low equilibrium water content (EWC).

Low extraction percentage is desired because a low extraction indicates that there are less unreacted monomers in the system. Extraction is the inverse of conversion: a high conversion (meaning all the monomers have been converted/reacted) produces a low extraction percentage. A low extraction is also a good prediction of a biocompatible material.

The glass transition temperature, T_g , is variable, but a T_g lower than room temperature is desirable. In the case of a dual T_g material, at least one of the T_g s should be lower than room temperature. A material with low T_g is soft at room temperature. However, if the T_g is too low, the material will become tacky.

An acceptable lens, upon curing the polymer composition, has 98% or more conversion, actual shrinkage percentage close to zero (0%) (for example, less than 10%, or less than 5%), low or no tackiness, low extraction (e.g., less than 3%), the material is glistening free, and the EWC is less than 15%, in some implementations less than 5%.

Lens 10 is formed from a polymeric material that includes at least one urethane-based acrylate. In some implementations, at least two urethane-based acrylates are present in the uncured polymeric composition.

The urethane-based acrylate may be an acrylate, a diacrylate, a triacrylate, a tetracrylate, etc. It may be, for example, aliphatic or aromatic. The acrylate may be long-chain (e.g., having 13 to 25 carbon atoms) or may be short-chain. Urethane-based acrylate(s) are preferred because they enable secondary interactions (reversible hydrogen bonding) within the composition. In some implementations, high refractive index polymer(s) (HRIP) and/or low refractive index polymer(s) (LRIP), either urethane-based acrylates or not, may be suitable in the polymer composition.

The urethane-based acrylate(s) is at least 10 wt-% of the total, uncured polymeric composition. In other implementations, the urethane-based acrylate(s) is at least 20 wt-% of the total, uncured polymeric composition, and in other implementations at least 25 wt-%. Still further, the urethane-based acrylate(s) can be at least 30 wt-%, or at least 35 wt-%, or at

least 40 wt-%, or at least 45 wt-%, or at least 50 wt-%, or at least 55 wt-%, or at least 60 wt-%, and in some implementations at least 65 wt-% of the total, uncured polymeric composition. Additionally, the urethane-based acrylate(s) is no more than 99 wt-% of the total, uncured polymeric composition, in some implementations no more than 98 wt-%.

5 In one particular implementation, the urethane-based acrylate(s) is 65-75 wt-% of the total, uncured polymeric composition, e.g., 67-72 wt-%.

It is noted that other monomer, polymer or copolymer materials may be used in place of the urethane-based acrylate(s), as long as they provide secondary interactions (reversible hydrogen bonding) in the composition and that the cured composition meets the criteria for a
10 lens.

The polymeric composition can include other acrylates in addition to the urethane-based acrylate(s); examples include diacrylates, triacrylates, acrylates, etc. that are non-urethane-based, such as methacrylates, ethylacrylates. If non-urethane based acrylate(s) are present in the polymer composition, the ratio of the urethane-based acrylate to the non-urethane based acrylate(s) is no more than 5, in other implementations no more than 4.5, in
15 other implementations no more than 4, and still in other implementations no more than 3.5 or no more than 3.0.

The polymeric composition can include other copolymer or monomer materials, including thermosetting materials (e.g., phenolics, epoxies, urea-formaldehydes, melamine formaldehydes, and the like) or thermoplastic materials (e.g., polyamides (nylon),
20 polyethylene, polypropylene, polyesters, polyurethanes, polyetherimide, polysulfone, polystyrene, acrylonitrile-butadiene-styrene block copolymer, acetal polymers, polyvinyl chloride, and the like). The composition can include other materials such as, for example, photoinitiator(s), plasticizer(s), catalyst(s), accelerator(s), activator(s), coupling agent(s),
25 lubricant(s), wetting agent(s), surfactant(s), UV blocker(s), UV stabilizer(s), and/or complexing agent(s). The polymeric composition can be 100% solids; that is, no solvent is present. In some implementations, however, the polymeric composition is composed of only acrylate(s).

The polymeric composition can be cured by an energy source that can be a source of
30 thermal energy or radiation energy, such as electron beam, ultraviolet light, or visible light. Electron beam radiation is also known as ionizing radiation. Ultraviolet radiation refers to radiation having a wavelength within the range of about 200 to about 400 nanometers, preferably within the range of about 250 to 400 nanometers. It is preferred that 118 to 400 mWatt/cm² ultraviolet lights are used. Visible radiation refers to radiation having a

wavelength within the range of about 400 to about 800 nanometers, preferably in the range of about 400 to about 550 nanometers. The amount of energy required is dependent upon the chemical nature of the reactive groups in the polymeric composition, as well as upon the thickness of the polymeric composition, for example, in the mold forming the lens. In other
5 implementations, the polymeric composition can be cured by an initiating system that can be a source of radicals, such as, e.g., thermal initiators, redox reactions, etc.

In some implementations, the polymeric compositions of this disclosure may be applied as a coating on previously prepared lenses or other ophthalmic devices and/or corneal prosthetics. Additionally, the copolymer formulation can be leveraged for storing and
10 delivering active molecules, such as biological and non-biological active molecules (e.g., drugs, biologics (e.g., peptides, aptamers etc.), with or without an associated coating that controls rate of delivery. The coating may be covalently bound to the copolymer material and may be composed of nano gels or other materials.

EXAMPLES: The following non-limiting examples were prepared. The objects,
15 features and advantages of the present invention illustrated in the following examples, which incorporate particular materials and amounts, should not be construed to unduly limit this invention. All materials are commercially available unless otherwise stated or apparent. All parts, percentages, ratios, etc., in the examples are by weight unless otherwise indicated.

The following abbreviations are used throughout the examples:

20 EB230 : aliphatic urethane-based diacrylate, commercially available under the trade name "Ebecryl 230;"

EB270 : aliphatic urethane-based diacrylate, commercially available under the trade name "Ebecryl 270;"

PEG : polyethylene glycol 400 (PEG 400), an extended urethane dimethacrylate;

25 EB350 : silicone diacrylate, commercially available under the trade name "Ebecryl 350;"

HEMA : hydroxyethyl methacrylate;

IBOA : isobornyl acrylate;

IBMA : isobornyl methacrylate;

30 MMA : methyl methacrylate;

TMPTA : trimethylol propane triacrylate;

HEA : 2-hydroxyl ethyl acrylate;

POSS : methacryl POSS silsesquioxane, also known as 2-propenoic acid, 2-methyl-3-(trimethoxysilyl)propylester, hydrolyzed;

EGMEA : ethylene glycol methyl ether acrylate;

PC : polycarbonate, based on oligocarbonate diols available from Bayer under the trade designation “Desmophene C2100” and 2-isocyanato ethylmethacrylate;

oMTP : 2-(2'-hydroxy-3'-methallyl-5'-methylphenyl)benzotriazole reactive UV absorber, commercially available as “o-Methallyl Tinuvin P” from Polysciences, Inc.;

Irg819 : bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide photoinitiator, available from BASF under the trade designation “Irgacure 819.”

Forty example polymeric formulations were prepared using the above-identified ingredients in the formulations identified in Tables 1 and 2. The formulations are identified as weight percentage of the total formulation.

Table 1

Ex.	EB230 wt-%	EB270 wt-%	MMA wt-%	TMTPA wt-%	HEA wt-%	POSS wt-%	Other
1	25	42	33	-	-	-	-
2	71.4	-	28.6	-	-	-	-
3	-	96.7	2.8	-	-	0.5	-
4	-	95.5	2.6	-	-	1.9	-
5	27.9	69.2	2.9	-	-	-	-
6	-	100	-	-	-	-	-
7	-	97.2	1.4	-	1.4	-	-
8	75.8	-	17.6		-	-	1.06% EGMEA; 0.03% EB350
9	71.3	-	22.9	5.7	-	-	-
10	-	97.2	1.4	1.4	-	-	-
11	23.1	45.9	21.4	9.6	-	-	-
12	-	94.4	5.6	-	-	-	-
13	81.7	-	1.7	16.6	-	-	-
14	-	96.4	1.2	2.4	-	-	-
15	-	96.7	-	-	3.3	-	-
16	25.2	41.5	-	-	33.3	-	-

Table 2

Ex.	EB230 (wt%)	EB270 (wt%)	MMA (wt%)	TMTPA (wt%)	HEA (wt%)	PEG (wt%)	IBOA wt%	IBMA (wt%)	PC (wt%)
17	27.80	46.20	26.00	-	-	-	-	-	-
18	30.00	50.00	20.00	-	-	-	-	-	-
19	37.00	37.00	26.00	-	-	-	-	-	-
20	34.00	42.00	24.00	-	-	-	-	-	-
21	40.00	34.00	26.00	-	-	-	-	-	-
22	60.00	15.00	25.00	-	-	-	-	-	-
23	50.00	25.00	25.00	-	-	-	-	-	-
24	28.00	48.00	20.00	-	-	4.00	-	-	-
25	71.30	-	23.00	5.70	-	-	-	-	-
26	23.00	46.20	21.50	9.20	-	-	-	-	-
27	25.00	42.00	-	-	33.00	-	-	-	-
28	-	35.00	-	-	31.00	34.00	-	-	-
29	28.00	46.00	-	-	-	-	26.00	-	-
30	28.00	46.00	-	-	-	-	-	26.00	-
31	40.00	34.00	-	-	-	-	26.00	-	-
32	40.00	34.00	-	-	-	-	13.00	13.00	-
33	40.00	34.00	20.00	-	-	-	6.00	-	-
34	40.00	34.00	23.00	-	-	-	3.00	-	-
35	32.00	42.00	23.00	-	-	-	3.00	-	-
36	27.00	47.00	23.00	-	-	-	3.00	-	-
37	-	46.20	25.90	-	-	-	-	-	27.70
38	-	46.00	-	-	26.00	-	-	-	28.00
39	-	29.60	-	-	25.90	16.6	-	-	27.70
40	-	40.30	-	-	22.60 (HEMA)	12.90	-	-	24.20

To each of the formulations in Table 2, 1.8 wt-% of oMTP (UV absorber) and
5 0.2 wt-% Irg819 (photoinitiator) were added.

The ratio of the urethane-based acrylate (i.e., E230, E270, PEG) to non-urethane-based
acrylate (i.e., E350, MMA, TMPTA, POSS, HEA, EGMEA, etc.) for the examples is
provided in Table 3, below.

Table 3

Ex.	ratio of urethane acrylate to non-urethane acrylate
1	2.03
2	2.50
3	29.30
4	21.22
5	33.48
6	-
7	34.71
8	4.31
9	2.49
10	34.71
11	2.23
12	16.86
13	4.46
14	26.78
15	29.30
16	2.00
17	2.85
18	4.00
19	2.85
20	3.17
21	2.85
22	3.00
23	3.00
24	12.67
25	2.48
26	2.25
27	2.03
28	0.54
29	2.85
30	2.85
31	2.85
32	2.96
33	2.85
34	2.85
35	2.85
36	2.85
37	0.86
38	0.85
39	0.42
40	0.68

The following procedures were used to prepare the examples from the formulations identified in Tables 1 and 2.

MIXING:

Step 1. The initiators and monomers were mixed in the following order: any initiator,
5 monomer 1, monomer 2, and any other ingredient.

Step 2. Vortexing was started after the first liquid monomer was added. after each monomer was added, the vial was vortexed on 'high' on a standard vortexer for 5 minutes.

Step 3. After all the monomers and initiators had been added, the monomer mixture
10 was further placed in a water-bath at 45°C and stirred for 30 minutes at 1000 RPM in a standard 20mL vial. To ensure thorough mixing, the mixing speed was strong enough to create a vortex that extended all the way to the stir bar at the bottom of the vial.

Step 4. After thorough mixing, the vial was removed and confirmed that the exterior of the vial was completely dry.

Step 5. The monomer mixture was filtered through a 0.45 micrometer disposable PES
15 membrane filter.

MOLD ASSEMBLY & FILLING: The resulting monomer mixture was placed into a lens mold. The mold was assembled in a clean environment free from dust, debris and other
20 particles that could potentially contaminate the mold and the monomer mixture. Powderless gloves were worn while assembling the molds.

CURING PROCEDURE:

Step 1. An Omnicure S2000 light source was assembled as follows: A liquid-filled
25 light guide was attached to the Omnicure S2000 light source. The distal end of the light guide was threaded through the aluminum support tube so that the tube at the end of the light guide stuck out of the aluminum tube by $\frac{1}{4}'' - \frac{1}{2}''$. The collimating adapter was attached to the end of the light guide at a distance of 7.25 mm from the shoulder of the guide. The 12.5 LP Filter-Collimating adapter was attached to the end of the collimating adapter and was fastened in
30 place by tightening the top set screw. A 425 nm cut-off filter was placed in the end of this adapter and fastened into place by tightening the lower set screw. The engineered diffuser was screwed into the 1" diameter optic mount. The optic mount slid over the 12.5 mm LP Filter-collimating adapter piece and was held in place by a set screw. The distal end of the

light guide assembly was oriented 27.5 mm from the surface on which the mold will be placed.

Step 2. The power to the S2000 light source was turned on and the light was warmed up for 30 minutes.

5 Step 3. A light intensity probe was centered directly under the light source. The shutter was opened to expose the probe.

Step 4. The intensity setting was adjusted until the Radiometer read 320 mW/cm^2 (approximately setting #44).

10 Step 5. The shutter was closed and a filled mold was placed under the light. Care was taken to center it directly under the filtering-diffuser assembly.

Step 6. The shutter on the light source was opened to expose the monomer mixture for 10-15 minutes, or until conversion was $\geq 98\%$.

Step 7. The shutter on the light source was shut and any paper clips holding the mold were removed.

15 Step 8. The mold was placed in a 90°C oven for about 10 minutes.

Step 9. The mold was removed from the oven and the polymer button was removed from the mold.

Step 10. The polymer button was now ready to undergo an extraction procedure to remove unreacted monomers, oligomers, and other impurities.

20

EXTRACTION PROCEDURE: To calculate the Extraction % associated with a particular example formulation, the initial and final masses of a sample button were measured before and after the extraction process. The mass was taken at Step 1 and at 24 hour increments during Step 8 to calculate mass loss.

25 Step 1. Placed one button in 30mL glass jar.

Step 2. Filled jar with 20mL acetonitrile (98% pure, Sigma Aldrich).

Step 3. Sealed jar with cap and placed sealed jar in 35°C oven for 72 hours.

Step 4. Removed jars from oven and drained acetonitrile.

30 Step 5. Placed cap with 0.25" hole on jar to allow venting of sealed jar (i.e., to slow evaporation rate).

Step 6. Left jars in fume hood at room temperature for 24 hours until buttons returned to original size.

Step 7. Removed vented caps and placed jars in 60°C vacuum oven.

Step 8. After buttons reached 60°C, mechanical vacuum was applied for 72 hours while still at 60°C.

Step 9. Removed buttons and cooled to room temperature.

5 The following procedures were used to determine various material and physical characteristics of the cured buttons (lenses).

CONVERSION PERCENTAGE (%): The following equipment was used: FTIR Mid Range, a laptop installed with Omnic software, and two pre- and post- light cure
10 samples.

Step 1. Turned on FTIR power supply, plugged in USB to laptop and opened Omnic Software.

Step 2. Set up Experimental Setup. Collect 16 scans in the Absorbance mode.

Step 3. Collected Background for sample.

15 Step 4: Ran example button sample before light cure. Saved Run and Added to Window.

Step 5. Ran example button sample after light cure. Saved Run and Added to Window.

20 Step 6. Compare the 6160 cm⁻¹ FTIR peak for the 'before light cure' and the 'after light cure' samples.

Step 7. Determined the area under peak using the area tool.

Step 8. Calculated % conversion by:

$$\% \text{ Conversion} = \frac{\text{Initial Area} - \text{Final Area}}{\text{Initial Area}} * 100$$

25 EXTRACTION MASS LOSS PERCENTAGE (%): The following equipment was used: high accuracy scale and three cured buttons (lenses).

Step 1. After button was fully cured and removed from mold, the initial mass of button was recorded.

Step 2. After the button had undergone the full extraction procedure, the final mass of the button was recorded.

30 Step 3. Calculated the mass loss percentage by:

$$\text{Extraction Mass Loss}\% = \frac{\text{Initial Mass} - \text{Final Mass}}{\text{Initial Mass}} * 100$$

EQUILIBRIUM WATER CONTENT (EWC): This test was used to determine swelling or water uptake of the cured material. It is desired to have a take up less than 4%. The following equipment was used: high accuracy scale, incubator, vacuum oven, and an example formulation test coupon.

- 5 Step 1. After the extraction calculation, punched coupons from button (lens).
- Step 2. Placed one coupon in 0.5 dram vial and labeled vial.
- Step 3. Measured initial dry mass of coupon.
- Step 4. Filled vial $\frac{3}{4}$ full with filter DI water and capped the vial.
- Step 5. The coupon was soaked for 5 days in the incubator at 35°C.
- 10 Step 6. Forceps were used to remove the soaked coupon from the vial. The surface of the coupon was dried by thoroughly dabbing on a wipe. The coupon was moved to a new dry place on the wipe and the wipe was folded over on top of the coupon. The wipe was then unfolded and the wet mass of the wipe was recorded.
- Step 7. The cap was removed from the vial and excess water was removed. The
- 15 coupon was dried at full vacuum at 60°C for 5 days.
- Step 8. Calculate EWC from the dry mass and the final weight by:

$$EWC = \frac{Wet\ Mass - Final\ DryMass}{Wet\ Mass}$$

REFRACTIVE INDEX (RI). This test was used to determine the refractive index of the material. It is desired to have RI > 1.4700 and ABBE > 50. The following equipment

20 was used: water bath and RI equipment, incubator, vacuum oven, and an example formulation test coupon.

- Step 1. After the extraction calculation, punched coupons from button (lens). For some runs, the same coupons used for the Extraction were used for the RI test.
- Step 2. Determined Dry RI value by: Turned on water bath to 35°C and set light to
- 25 setting 7. Once digital thermometer read RI to be at 35°C, placed coupon in the middle of the prism. Used the back of a set of forceps to ensure good surface contact. Closed lid and waited approximately 30 seconds to ensure that the coupon has reached 35°C. Then, looked through the eye piece and focused equipment. Recorded value to the 4th digit (i.e., RI=1.4700).
- 30 Step 3. Placed one coupon in 0.5 dram vial and labeled vial.
- Step 4. Measured initial dry mass of coupon.
- Step 5. Filled vial $\frac{3}{4}$ full with filter DI water and capped the vial.
- Step 6. The coupon was soaked for 5 days in the incubator at 35°C.

Step 7. Determined Wet RI value by: Turned on water bath to 35°C and set light to setting 7. Once digital thermometer read RI to be at 35°C, removed coupon from vial and dried off surface. Placed dry coupon in the middle of the prism. Used the back of a set of forceps to ensure good surface contact. Closed lid and waited approximately 30 seconds to ensure that the coupon has reached 35°C. Then, looked through the eye piece and focused equipment. Recorded value to the 4th digit (i.e., RI=1.4700).

Step 8. The cap was removed from the vial and excess water was removed. The coupon was dried at full vacuum at 60°C for 5 days.

Step 9. If any additional dry RI values were desired, the procedure of Step 2 was repeated.

GLISTENING PROCEDURE. Having an acceptable glistening effect is important for lenses, particularly intraocular lenses. The glistening effect is affected by both the formulation and the manufacturing process. Additionally, factors such as cross-linking density, Tg, extraction %, and the relative hydrophobicity/hydrophilicity can all have an effect. The following equipment was used as a qualitative test for glistening: high powered microscope, incubator, and an example formulation test coupon.

Step 1. After the extraction calculation, punched coupons from button (lens).

Step 2. Placed one coupon in 0.5 dram vial and labeled vial.

Step 3. Filled vial $\frac{3}{4}$ full with filter DI water and capped the vial.

Step 4. Placed vial in 45°C incubator for 24 hours.

Step 5. Removed vials from incubator and immediately placed coupons in 37°C water bath to induce shock factor.

Step 6. Left coupons in water bath for 10 minutes, or until they reached equilibrium water bath temperature.

Step 7. Qualitatively analyzed glistening property by viewing coupons under high powered microscope.

Step 8. Steps 2-4 were repeated and the vials were removed from the incubator and placed in a water bath at room temperature and analyzed for glistening.

Step 9. Identified sample as “glistening free - yes” if no to minimal signs of glistening, or “glistening free - no” if visible dust, particles, or other debris present.

TACKINESS. The tackiness or stickiness of the sample was evaluated by the following qualitative tests. In Test #1, a cured polymeric sample (button, lens) was manually

folded. A value from 1 to 10 was qualitatively assigned based on the time necessary for the sample to unfold and the manner of unfolding, where 1 was best unfolding and thus least tacky. In Test #2, a cured polymer sample was brought in contact with a pair of metal tweezers to assess the propensity of the material to adhere to a metal surface. A qualitative assessment of the material's response was noted.

% LIGHT TRANSMITTANCE. For an intraocular lens or other ophthalmic use, the % light transmittance of the polymeric material is desired to be at least 85%. The % transmittance of the polymeric sample was evaluated using UV visible spectroscopy. Polymer slabs were attached onto the surface of a quartz cuvette and carefully introduced into the sample compartment of the spectrometer. Light in the range of 200-800 nm was passed through the polymer strips and % transmittance through each strip was recorded.

ABBE NUMBER. The Abbe number, also known as the V-number or constringence of a transparent material, is a measure of the material's dispersion (variation of refractive index versus wavelength, with high values indicating low dispersion).

MECHANICAL PROPERTIES OF THE POLYMER: ULTIMATE STRESS, STRAIN AND YOUNG'S MODULUS. The mechanical properties of the material were assessed and quantified. An MTS Insight™ Material Testing System with a 2kN load cell was used to quantify the ultimate strain, stress and Young's modulus of the polymer samples.

Various examples from Tables 1 and 2 was evaluated using the procedures described above. The results are provided below in Tables 4 and 5 and in FIGS. 2, 3 and 4.

Table 4

Ex.	Conversion %	Theoretical Volume Shrinkage %	Dry RI	Wet RI	Tack Test #1	Extraction %	Tg (°C) (DSC)	Free of glistening	EWC %
1	98.9	8.89	1.484	1.481	2	1.72	-16	Yes	3.30
4	99.2	3.93	1.484	1.481	6	0.89	-15	No	3.94
5	99.9	3.16	1.479	1.476	7	1.3	-16	No	3.24
9	99.6	7.22	1.476	1.474	5	3.3	-16	Yes	3.84
10	98.4	3.74	1.484	1.481	1	1.24	-17	No	2.46
11	99.5	8.81	1.485	1.483	4	1.31	-17	Yes	2.85
12	99.9	3.97	1.487	1.482	3	1.84	-15	No	2.62
14	99.8	3.97	1.484	1.481	8	0	-16	No	3.13
15	99.1	3.77	1.483	1.479	-	1.18	-13	No	3.84

16	99.8	8.22	1.483	1.478	-	2.38	6	Yes	14.03
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Table 5

	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21	Ex. 22	Ex. 23
% Conversion	99.3	99.8	99.1	98.9	98.6	99	99.2
% Extraction	0.66	-	-	-	-	-	-
Tack Test #2	Good	Good	Good	Good	Good	Good	Good
Clarity	Clear	Clear	Clear	Clear	Clear	Clear	Clear
EWC (35°C, BSS), %	2.42±0.04	2.68±0.06	2.57±0.12	2.72±0.04	3.1±0.19	4.23±0.11	-
Refractive index @35°C and 589 nm	1.4765 ± 0.0005	1.4758 ± 0.0004	1.4716 ± 0.0003	1.4731 ± 0.0008	1.4722 ± 0.0005	-	-
Abbe No.	54.6±0.9	53.9±1	55.3±2.6	56.6±2.7	54.9±0.66	-	-
Free of Glistening	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Stress at break, MPa	6.51±0.62	6.68±0.54	4.02±0.35	6.36±0.84	5.44±1.3	-	-
Strain at break, %	94.4±4.7	79.3±11.5	49.3±5	66.5±8.21	83.2±21	-	-
Young's Modulus, MPa	33.51±3.63	47.93±5.26	24.97±4.58	38.27±3.87	50±7.2	-	-
25% Secant Modulus, MPa	8.49±0.74	11.28±1.14	9.61 ±0.48	12.10±0.57	9.42±0.43	-	-
100% Secant Modulus, MPa	6.88	NA	NA	NA	6.25	-	-

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FIG. 2 (labeled “A”) is a microscopic image of the polymer slab from Example 21 showing no glistening.

FIG. 3 (labeled “B”) is a microscopic image of the polymer slab from Example 37 showing glistening.

10 FIG. 4 shows the % transmittance for clear, sample holder; a standard acrylate-based intraocular lens formulation (which includes oMTP), 1.0 mm thick; Example 21 (with oMTP), 0.82 mm thick; and Example 21 but without the oMTP, 0.84 mm thick.

The above specification, examples, and data provide a complete description of the structure, features and use of exemplary implementations of the invention. Since many
15 implementations of the invention can be made without departing from the spirit and scope of the invention, the invention resides in the claims hereinafter appended. Furthermore,

structural features of the different implementations may be combined in yet another implementation without departing from the recited claims.

WHAT IS CLAIMED IS:

1. A polymeric composition for a lens, the composition comprising urethane-based acrylate.
- 5 2. The polymeric composition of claim 1, comprising at least 50 wt-% urethane-based acrylate.
3. The polymeric composition of claim 1, comprising at least 60 wt-% urethane-based acrylate.
- 10 4. The polymeric composition of claim 1, comprising the urethane-based acrylate and non-urethane based acrylate.
5. The polymeric composition of claim 4, wherein a ratio of the urethane-based acrylate and
15 non-urethane based acrylate is no more than 3.5.
6. The polymeric composition of claim 1, comprising 65-75 wt-% urethane-based acrylate.
7. The polymeric composition of claim 1, comprising 67-72 wt-% urethane-based acrylate.
- 20 8. The polymeric composition of claim 1, configured to be applied as a coating on a lens.
9. A lens made from the polymeric composition of any of claims 1-7.
- 25 10. The lens of claim 9, being an intraocular lens.
11. The lens of claim 9, being a contact lens.
12. The lens of claim 9, being a corneal prosthetic other than an intraocular lens or contact
30 lens.

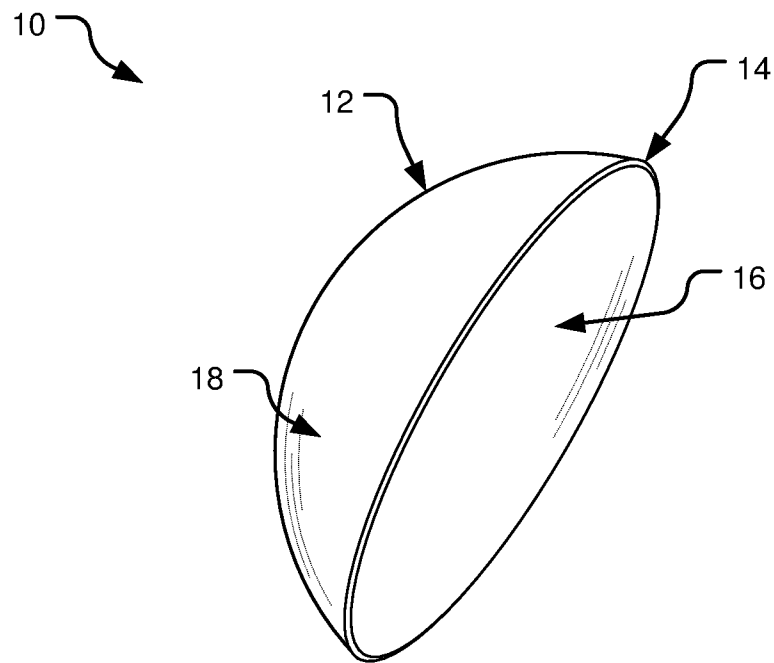


FIG. 1

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FIG. 2

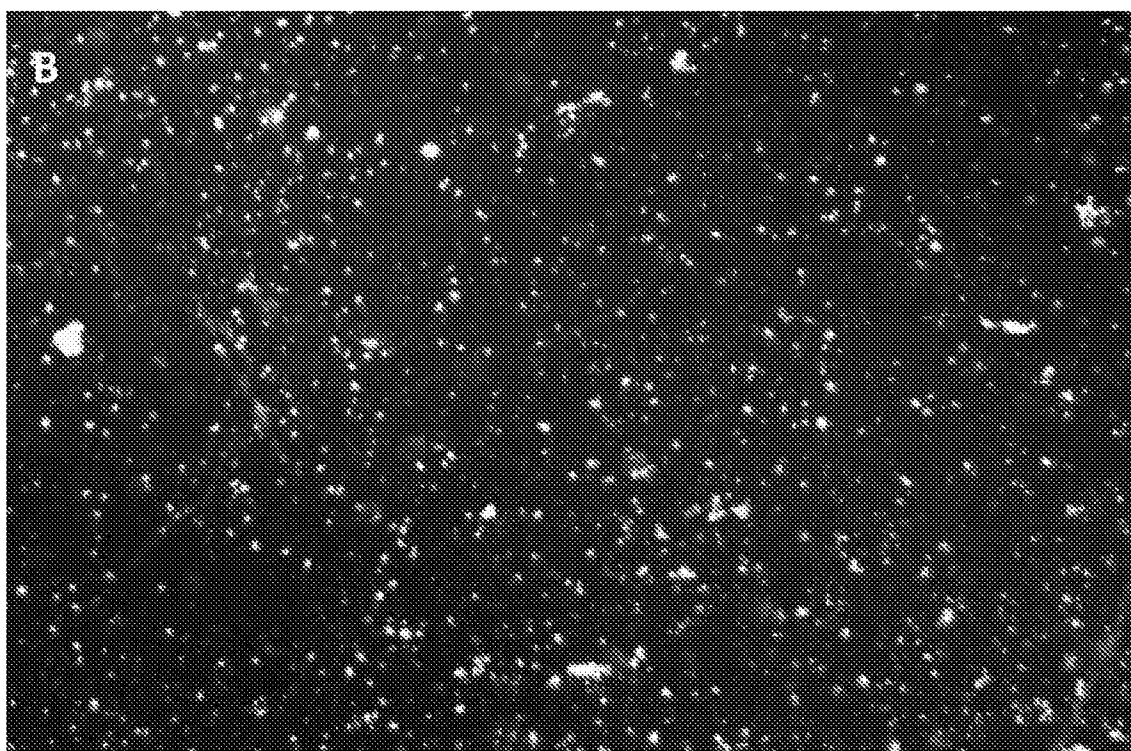


FIG. 3

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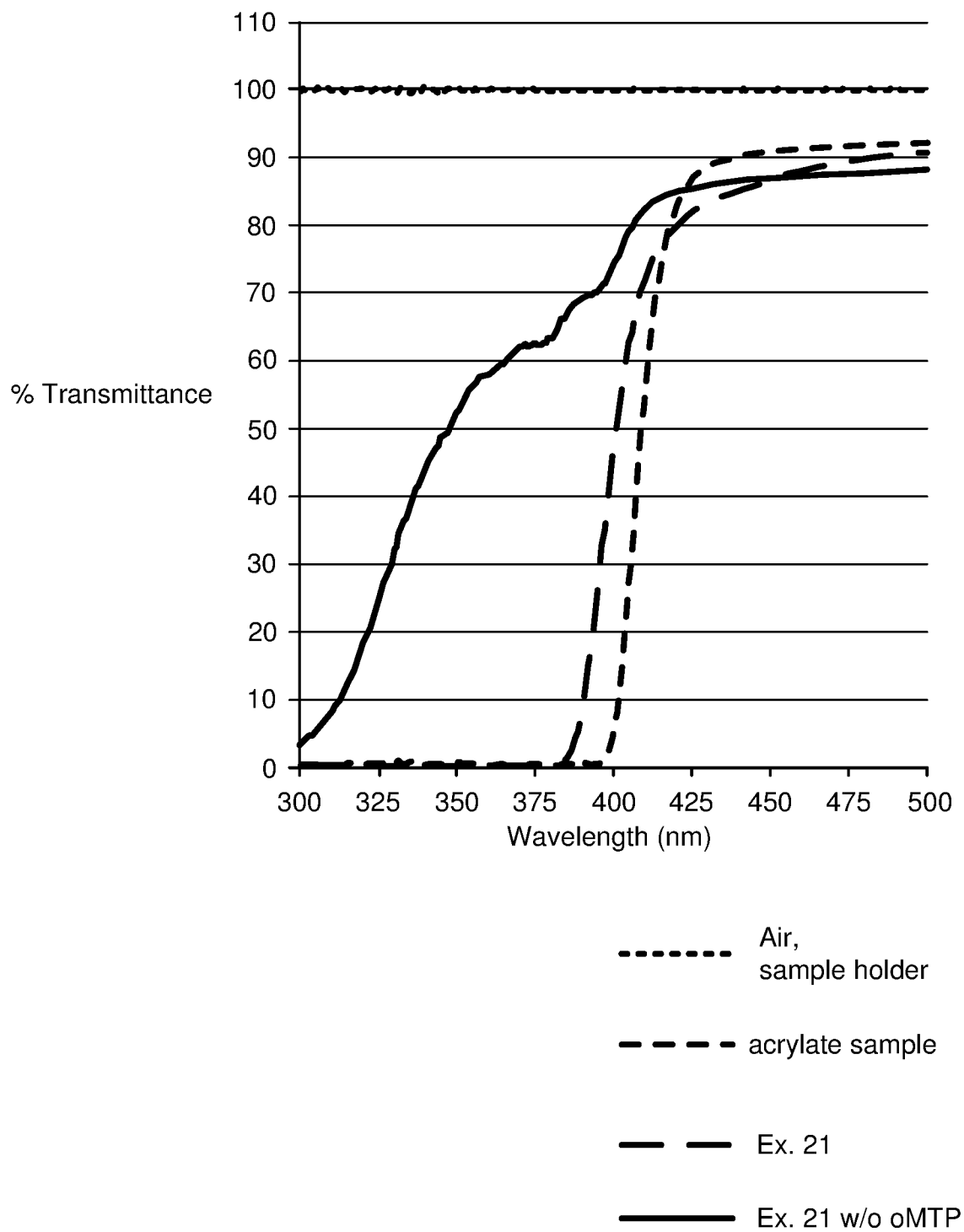


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US16/13675

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - G02B 1/04; G02C 7/02; A61F 2/14 (2016.01)

CPC - G02B 1/041; G02C 7/02; A61F 2/14

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)

IPC(8): G02B 1/04, 1/10, 3/00; G02C 7/02; A61F 2/14 (2016.01)

CPC: G02B 1/041, 1/10; G02C 7/02; A61F 2/14; C08G 18/8116

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); IP.com; Google/Google Scholar; EBSCO; lens, polymer, copolymer, urethane, acrylate, percent, monomer, comonomer, coat, intraocular lens, contact lens, corneal prosthetic, corneal implant, corneal transplant

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 4,543,398 A (BANY, SW et al.) 24 September 1985; column 4, lines 35-39; claims 1, 4-5, 16, 29, 31	1-7, 9/1-7, 10/9/1-7, 11/9/1-7, 12/9/1-7 ----- 8
Y	KR 2011/0050952 A (KCC CORP) 17 May 2011; see English translation; abstract; page 3	8
A	US 5,556,929 A (YOKOYAMA, Y et al.) 17 September 1996; entire document	1-8, 9/1-7, 10/9/1-7, 11/9/1-7, 12/9/1-7
A	JP 2007/086389 A (NOF CORP) 05 April 2007; see English translation; entire document	1-8, 9/1-7, 10/9/1-7, 11/9/1-7, 12/9/1-7
A	JPH 0,797,511 A (HOYA CORP) 11 April 1995; see English translation; entire document	1-8, 9/1-7, 10/9/1-7, 11/9/1-7, 12/9/1-7
A	JPH 06,123,858 A (TOKYO KEIKAKU KK) 06 May 1994; see English translation; entire document	1-8, 9/1-7, 10/9/1-7, 11/9/1-7, 12/9/1-7

☐ 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

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"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

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"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

02 March 2016 (02.03.2016)

Date of mailing of the international search report

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