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SPECIFICATION

ULTRAVIOLET ABSORBING POLYMER COMPRISING FULLERENE

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ULTRAVIOLET ABSORBING POLYMERS COMPRISING FULLERENE

BACKGROUND OF THE INVENTION

This invention relates to ultraviolet light absorbing polymer compositions, and more particularly, to polymer composition comprising copolymers of fullerenes with one or more other monomers copolymerizable therewith, particularly acrylic monomers. This invention further relates to ocular devices, particularly sunglasses, intraocular lenses and contact lenses, prepared from such ultraviolet light absorbing polymers.

The absorption of radiation in the ultraviolet region by polymeric materials is a major cause of the light induced degradation therein. It is standard practice to add a low molecular weight UV "stabilizer" to light sensitive polymers to absorb the light in the destructive range or to quench the energy generated as a result of the excitation of the light absorbing functional groups in the polymer.

Although low molecular weight UV absorbers or quenchers of various types are effective in inhibiting or retarding the destruction of the polymers to which they are added, their extractibility in various media and/or their volatility during the processing or fabrication of the polymer at elevated temperatures place a limitation on their utility.

This problem has been remedied to a considerable extent by the synthesis of copolymerizable monomers containing structural features capable of functioning as a UV absorber or quencher. The copolymerization of such monomers results in the formation of copolymers with increased stability, i.e., resistance to degradation upon exposure to UV light with decreased extractibility and volatility.

US Pat. No. 4,304,895 discloses the use of 2-hydroxy-4-methacryloyloxybenzophenone and mixtures thereof as a monomeric UV absorber copolymerizable with acrylic monomers and useful in the preparation of UV absorbing hard contact lenses.

Similarly, copolymerization of an allyl-2-hydroxy-benzophenone with an acrylate ester such as methyl acrylate is described in U.S. Pat. No. 4,310,650, and, the copolymerization of ethylenically unsaturated derivatives of 2,4-dihydroxy benzophenone with other vinyl type comonomers is broadly disclosed in U.S. Pat. No. 3,162,676.

U.S. Pat. No. 4,528,311 discloses certain benzotriazole monomers which are copolymerizable with vinyl monomers such as methyl methacrylate to yield optically clear polymers useful in the preparation of intraocular and contact lenses. Representative of the disclosed benzotriazole monomers and a particularly preferred compound is 2-(2'-hydroxy-5'-methacroyoxypropyl-3'-tert-butylphenyl)-5-chloro-2H-benzotriazole.

The problem of eye damage caused by the penetrating UV radiation in the 300-400 nm range is especially acute in aphakic patients. Aphakic patients have lost their natural lens, which is the primary UV filter in the eye. Without this natural UV filter, aphakic patients are far more susceptible to the photochemical damage that long range UV light can induce. The visual correction of aphakia resulting from such lenses removal requires the use of

high plus corrective lens which may be in the form of spectacles, contact lens or intraocular lens

Intraocular lenses and hard contact lenses are presently produced from methacrylate polymers which exhibit a combination of properties desirable for such products, particular optical clarity, the capability of being cut and polished to specific optical powers, and chemical inertness. UV absorbing lenses of polymethylmethacrylate (PMMA) are required to maintain these properties while achieving at least 85% absorption of light to 400 nm based on a polymer film of thickness 1mm.

While the benzotriazole monomers described in U.S. Pat. No. 4,528,311 are effective UV absorbers and form chemically stable copolymers with, for example, methyl methacrylate, a concentration of about 3% of the monomer in the copolymer is required to provide the desired degree of absorption to 400 nm. The absorption of such copolymers cuts off sharply above 400 nm so that very little light in the 400 to 450 nm range is absorbed. As a consequence, lenses of PMMA copolymers do not demonstrate the same absorption characteristics as the natural lens of an elderly person who is the most frequent recipient of an intraocular lens.

U.S. Pat. No. 4,716,234 claimed that the benzotriazoles of their invention are far more effective UV light absorbers than those of prior art in terms of the much lower amount of absorber required to achieve a similar transmittance characteristic as compared to that claimed in U.S. Pat. No. 4,528,311.

Molecular fullerenes have been described as entirely closed, hollow spheroidal shells of carbon atoms containing 32 to 1000 or more carbon atoms in each sphere, reference Smalley, R.E. "Supersonic Carbon Cluster Beams in Atomic and Molecular Clusters", Bernstein, E.R. Ed.; Physical and Theoretical Chemistry, Vol.68, Elsevier Science: New York, 1990; pages 1 to 68, the disclosure of which is totally herein by reference. The prototypical fullerene, C₆₀, has been referred to as buckminsterfullerene and has the molecular geometry of a truncated icosahedron, thus the C₆₀ molecules resemble a molecular sized soccer ball, reference Time Magazine, May 6, 1991, page 66, and Science, vol.22, Apr.12, 1991, page 646, the disclosure of which is totally incorporated herein by reference. Molecules of C₆₀ as well as C₇₀ and other fullerenes have also been referred to as buckyballs. Buckminsterfullerenes are usually comprised of C₆₀ molecules contaminated with small amount of C₇₀ and possibly C₈₄ molecules or even smaller

amounts of higher molecular weight fullerene molecules. The preparation of buckminsterfullerene and other fullerenes from the contact arc vaporization of graphite and a number of the buckminsterfullerene characteristics such as solubility, crystallinity, color and the like have been described in Kratschmer, et al., Nature, 1990, vol.347, pages 354 to 358, the disclosure of which is totally incorporated herein by reference. The fullerene mixture used in this invention is from Texas Fullerenes Corporation, Houston, Texas, USA, and is believed to be comprised mainly of C_{60} and smaller amounts of C_{70} and C_{84} carbon molecules, and possibly small amounts of other higher molecular weight fullerenes. Pure C_{60} can be separated from the mixture by chromatography using hexane as solvent and is designated as fullerene in this invention.

SUMMARY OF THE INVENTION

It is accordingly an object of the present invention to provide a ultraviolet absorbing composition comprising a polymeric material and fullerene or fullerenes mixture with improved UV absorption characteristics for use in sunglasses, intraocular and contact lenses. It is a further object to provide a new composition of matter, which, when copolymerized at extremely low concentrations with other monomers, effectively absorb at least 99% of incident light below 420 nm at 4 mm thickness. It is a further object to provide a composition which absorbs UV light in the range of 300 to 400 nm more effectively than prior art materials. These and other objects of the present invention will be apparent from the ensuing description and claims.

Specifically, the fullerenes, a third form of carbon, have been described as being comprised of 60 atom clusters of carbon arranged at the vertices of a truncated icosahedron and resembling miniature soccer balls. Reference to fullerenes includes all forms of the fullerenes illustrated herein, other known fullerenes, mixtures thereof in embodiments, and the like.

DESCRIPTION OF THE DRAWINGS

FIG.1 is a plot of transmittance curves of polymethylmethacrylate copolymers with increasing amount of fullerene.

FIG.2 is a plot of UV transmittance curves for polymethylmethacrylate copolymers with increasing amount of fullerenes mixture.

EXAMPLE 1

Polymerization

In a 10 mL round-bottom flask, fullerene (pure C₆₀) powder (2.88 mg), 5 mL of methyl methacrylate (MMA) were added together and polymerized with 0.25% by weight of azobisisobutyronitrile (AIBN) as initiator at 85°C. This composition yields a fullerene concentration of 0.03% by weight.

Initially, only a little of the fullerene dissolved in MMA, showing a purple solution. About 0.5 hour later, all of the fullerene dissolved in MMA. A clear yellow colored solution was observed. When the monomer became viscous, it was carefully poured into the cell which was made of two sheets of glass and a Teflon frame sandwiched between the plates using the spring clips to retain it in position. It was then placed vertically in an oven at 45°C for about 15 hours, then at 90°C for two hours. When cooled, the clear sheet of PMMA-fullerene could strip easily on removing the spring clips. The result polymer showed transmission of 79.9% at 700 nm, 3.3% at 430 nm and 0.00% at 400 nm. A UV-transmittance curve for the polymer in Example 1 containing 0.03% by weight together with curves of similarly prepared polymer containing from 0.002 to 0.06 percentage of the fullerene is shown in Fig. 1. It can be observed that even as low as 0.015% addition of fullerene, only 3.2% of the light is transmitted at 400 nm. As the concentration of fullerene is increased, substantial complete absorption occurs to above 480 nm. It is possible to regulate the amount of light in the range of 380 to 430 nm by varying the concentration of fullerene in the composition.

For optical UV filtering in sunglasses or ocular lenses, strong absorption of light up to about 420 nm is desired. This can be achieved in the present invention from as low as 0.03% of fullerene, as compared to the much higher level required claimed in prior arts. For example, U.S. Patent 4,716,234 requires a loading of 3.0% of a benzotriazole UV absorber to achieve transmission of 29% at 430 nm and 0.08% at 400 nm. A 0.03% loading of fullerene in the present invention absorbs all the light at 400nm and only transmits 3.3% at 430 nm.

For the composition in Example 1, the quantitative amount of UV light cut off between 300 to 400 nm is tabulated as follows :

Fullerene wt%	0	0.002	0.004	0.008	0.015	0.03	0.06
UV cut-off (300-400 nm).	58%	77%	83%	95%	99%	99.8%	100%

Example 2 Polymerization

In a 10-mL round-bottomed flask, 1.44 mg of a fullerenes mixture (obtainable, for example, from Texas Fullerenes Corporation, and believed to be comprised of mainly C₆₀ and smaller amounts of C₇₀ and C₈₄ carbon molecules, and possibly small amounts of other higher molecular weight fullerenes), 5 mL of methyl methacrylate (MMA) were added together and polymerized with 0.25% by weight of azobisisobutyronitrile (AIBN) as initiator at 85°C. This composition yields a fullerenes mixture concentration of 0.03% by weight. When the monomer became viscous, it was carefully poured into the cell which was made of two sheets of glass and a Teflon frame sandwiched between the plates using the spring clips to retain it in position. It was then placed vertically in an oven at 45°C for about 15 hours, then at 90°C for two hours. When cooled, the clear sheet of PMMA-fullerenes mixture could strip easily on removing the spring clips. The resulting polymer showed transmission of 77.3% at 700 nm, 6.2% at 430 nm and 1.0% at 400 nm. Again the 0.03% loading by weight of fullerenes mixture easily outperforms those UV absorbers claimed in prior arts. Fig.2 shows the UV absorption characteristics of PMMA with increasing concentration of fullerenes mixture.

Example 3

In a 10 mL round-bottom flask, a fullerenes mixture (0.72 mg), 4.6 mL of methyl methacrylate (MMA) and 0.4 mL of ethyl methacrylate (EMA) was polymerized with 0.25% by weight of azobisisobutyronitrile (AIBN) as initiator at 85°C. This composition yields a fullerene concentration of 0.015% by weight. When the monomer became viscous, it was carefully poured into the cell which was made of two sheets of glass and a Teflon frame sandwiched between the plates using the spring clips to retain it in position. It was then placed vertically in an oven at 45°C for about 15 hours, then at 90°C for two hours. When cooled, the clear sheet of PMMA-fullerenes mixture could strip easily on removing

the spring clips. The resulting polymer showed transmission of 77.3% at 700 nm, 6.2% at 430 nm and 1.0% at 400 nm.

The fullerene and fullerenes mixture may be copolymerized with any of a number of unsaturated monomers to provide the polymeric composition having desirable UV absorbing characteristics. Representative of the polymers and copolymers useful in conjunction with fullerene and fullerenes mixture are :

- a. Polymers which are derived from mono- or diolefins, eg., polyethylene which can optionally be crosslinked polypropylene, polyisobutylene, polymethylbutene-1, polymethylpentene-1, polyisoprene, polybutadiene.
- b. Mixtures of the homopolymers cited under (a), for examples mixtures of polypropylene and polyethylene, polypropylene and polybutylene-1, polypropylene and polyisobutylene.
- c. Polystyrene
- d. Copolymers of styrene and α -methylstyrene, for example styrene/butadiene copolymers, styrene/acrylonitrile copolymers, and styrene/acrylonitrile/methacrylate copolymers.
- e. Halogen containing vinyl polymers, for example polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, vinyl chloride/vinylidene copolymers, vinyl chloride/vinyl acetate copolymers.
- f. Polymers which are derived from α,β -unsaturated acids and derivatives thereof, polyacrylates and polymethacrylates, polyhydroxyethylmethacrylate, polyacrylic amides and polyacrylonitrile.
- g. Polycarbonates.

- h. Polyamides and copolyamides which are derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, for example polyamide 6, polyamide 6/6, polyamide 6/10, polyamide 11, and polyamide 12.
- i. Polyesters which are derived from dicarboxylic acids and dialcohols and/or from hydroxycarboxylic acids or the corresponding lactones, for example polyethylene glycol terephthalate, poly-1,4-dimethylolcyclohexane terephthalate.
- j. Natural polymers, for example cellulose, rubber, as well as the chemically modified homologous derivatives thereof, for example cellulose acetate, cellulose propionates and cellulose butyrates and the cellulose ethers, for example methyl cellulose.

Particularly useful compositions are copolymers comprising from 0.01 to 0.1 % by weight of fullerene or fullerenes mixtures with other ethylenically unsaturated materials such as styrene, methylstyrene, siloxanes, acrylates, methacrylates, acrylamides, acrylonitrile, vinyl acetate, vinylidene chloride, vinyl chloride, vinyl fluoride, ethylene, propylene and mixtures thereof.

The composition of this invention finds wide applications in formulating UV absorbing plastics and other organic materials wherever such materials are exposed to UV radiation from either natural or artificial sources. In addition to the medical use in intraocular and contact lenses described above, the materials of the present invention are useful in many industrial applications such as in solar energy collectors, polymeric coatings, transparent plastic films, fluorescent light diffusers, packaging materials, vinyl window coverings, automobile paints and interior coverings, epoxys, fiberglass constructions and others. Many other applications will be apparent to those familiar with this art as a result of proceeding specification.

We claim :

CLAIMS



1. An ultraviolet light stabilized polymer composition comprising a fullerene or a fullerenes mixture.
2. The composition of claim 1 wherein the said polymer is selected from the group consisting of polyvinyl halides, polyacrylates, polymethacrylates, polystyrene, polyvinylidene halides, polyolefins and polycarbonates.
3. A composition in accordance with claim 1 wherein the fullerene is present in an amount of from between about 0.001 and about 0.1 weight percent.
4. A composition according to claim 1, which also contains one or more additional ingredients selected from among antioxidants, heat stabilizers, coloring agents, fillers, reinforcing agents, mold release agents, lubricants, melt viscosity reducers, flame retardants and synergists, and plasticizers.
5. A composition in accordance with claim 1 wherein the fullerene is comprised of C₆₀ carbon.
6. A composition in accordance with claim 1 wherein the fullerene is comprised of C₆₀ carbon in the configuration of a soccer ball.
7. A composition in accordance with claim 1 wherein the fullerene mixture is comprised of C₆₀ carbon, C₇₀ carbon, C₈₄ carbon, C₂₃₄ carbon, C₃₄₀ carbon, or mixtures thereof.
8. A plastic film comprising the composition of claim 1.
9. A coating material comprising the composition of claim 1.