

Description

This invention is concerned with polymer compositions which are resistant to yellowing and/or loss of transparency on exposure to sterilizing radiation, such as gamma or electron beam irradiation, for sterilization purposes, to methods of making them and articles made from them.

Poly(methyl methacrylate), including clear, impact modified forms, is a useful polymer for forming articles in the medical field, such as syringes, spikes, connectors and luers, suction devices, urine meters, blood plasma separators, drip chambers, cuvettes, dialyzer casings, chest drainage units, bottles for fluids, vaginal speculums, flow valves, aspirators, pump housings, containers for operating instruments, as the polymers are crystal clear, easily molded into the desired form, compatible with poly(vinyl chloride) (PVC) tubing, bondable to other plastics, resistant to deformation under warm conditions, reasonably tough and readily processed into useful objects. Such objects further have dimensional stability, have design flexibility, and can readily be disposed of after one-time use by incineration.

For many uses in the medical field, sterilization of these articles is required. Sterilization is often accomplished by exposure of the article to low level gamma or electron beam radiation (which will be designated "sterilizing radiation"). This sterilization is usually done for "use-once" or throw-away articles, although this invention is also applicable to repeated use articles.

The amount of radiation utilized to accomplish sterilization is well above "background" radiation, and when objects of polymerized methyl methacrylate are exposed to such radiation, the polymer is subject to yellowing. This yellowing reduces the clarity of the poly(methyl methacrylate) and alters its appearance in an aesthetically unfavorable way. Much of the yellow color will be lost on aging, especially if the sterilized sample is maintained at an elevated temperature, such as about 60°C., but the level of residual color is still unattractive when compared to the non-irradiated sample.

Poly(methyl methacrylate), although far less prone to discolor and lose properties on exposure to sunlight than other plastics, may be further stabilized against discoloration and loss of properties by use of any of a variety of ultraviolet stabilizers, such as benzotriazoles, hydroxyphenylbenzotriazoles, hindered amines, such as derivatives of 2,2,6,6-tetramethylpiperidine, salicylate esters, such as phenyl salicylate, o-hydroxybenzophenones, and the like. However, these materials are ineffective against discoloration by sterilizing radiation and certain of them may indeed contribute further to such discoloration.

Attempts to improve gamma radiation resistance of poly(methyl methacrylate) by addition of propyl alcohol are known. An article by A.S. Belichenko et al, entitled "On the Mechanism of Polymer Destruction under UV and Gamma Irradiation: The Influence of Low Molecular Weight Additives Related to Vibrational Cross-Relaxation", Sixth Symposium on Radiation Chemistry, (1986), pages 535-538, discloses that polymer samples prepared by bulk radical polymerization of monomer compositions of methyl methacrylate which incorporated from 5 to 20% n-propyl alcohol showed improved resistance to gamma radiation, as judged by much slower development of UV-adsorbing chromophores. The large amounts of at least 5% propyl alcohol, however, would be expected to degrade the physical and mechanical properties of these polymers. This publication presents no comparative data between stabilized and non-stabilized polymers, but contrasts only irradiated and non-irradiated polymers of the same alcohol content in a qualitative statement.

Polymers of methyl methacrylate containing levels of non-polymerisable alcohols less than 0.5%, insufficient effectively to inhibit yellowing on exposure to sterilizing radiation, have been known for some years. We recently found polymers of methyl methacrylate containing similar amounts of similar alcohols as described in the present invention to be effective in resistance to ultraviolet degradation; such compositions are disclosed in our earlier copending EP-A-0371679. It is well-known that commercial ultraviolet stabilizers in poly(methyl methacrylate) may protect against ultra-violet degradation but are ineffective or even produce higher color on exposure to sterilizing radiation, such as gamma irradiation. Thus, there is no reason to anticipate similar stabilization behavior for alcohol-containing poly(methyl methacrylate) on exposure to differing types of radiation of differing wave lengths and energy.

Thus, the problem with which this invention is concerned is the stabilisation of poly(methyl methacrylate) and related polymers against discolorisation on exposure to sterilizing radiation, while maintaining other desirable physical properties.

In its broadest aspect this invention is concerned with the use of non-polymerisable aliphatic alcohol containing up to ten carbon atoms, in the absence or other ultraviolet stabiliser, to impart resistance to sterilising radiation to polymer comprising at least 50% by weight units of (C₁-C₄)-alkyl esters, cyclohexyl ester, or isobornyl ester of methacrylic acid and/or N-hydrogen or N-alkyl dimethylglutarimide, and, optionally other vinyl or vinylidene monomer units said alcohol being used in an amount of 0.5 to 2% by weight based on the weight of said polymer.

The polymeric object with improved resistance to sterilizing radiation can be produced by first mixing one or more monomers wherein the ester comprises at least 50% of the total monomer mix, with from about one-half to about two percent (by weight of the monomer) of non-polymerisable aliphatic alcohol having from one to ten carbon atoms, no ultraviolet stabilizer being present, free-radical polymerization initiator, and optionally mercaptan chain transfer agent, then polymerizing the resulting mixture to form a polymer comprising at least 50% ester units. The polymer may be used directly in the form in which it is polymerized; in other cases, it may be processed by methods well known to the art into an useful object resistant to sterilizing radiation.

The polymer may also be prepared separately and combined with the alcohol, no ultraviolet stabilizer being present, to form the desired blend, which is then processed by means well known to the art to form a useful object resistant to sterilizing radiation. The impact modifier may be admixed with the polymer prior to admixing the alcohol.

In this description by alkyl methacrylate, we mean (C_1 to C_4)-alkyl esters, the cyclohexyl ester, and the isobornyl ester. These polymers have sufficiently high glass temperatures to be rigid, hard glasses at temperatures of room temperature and above. Especially preferred is methyl methacrylate for lower cost and ease of polymerization of the monomer, and for the high glass temperature and ease of impact modification of the resultant polymer. It is further preferred for reasons of good initial color, thermal stability and high service temperature of the resultant polymer that the amount of methacrylate ester be from about 90 to about 99 weight percent of the monomer mixture to be polymerized.

A variety of other monomers, such as vinyl or vinylidene monomers, may be copolymerized with the alkyl methacrylate esters, for example, vinyl aromatic monomers, such as styrene and alpha-methylstyrene, acrylate esters, such as alkyl acrylate esters, for example, methyl, ethyl, n-propyl, n-butyl, s-butyl and 2-ethylhexyl acrylate, (meth)acrylic add, (meth)acrylonitrile, vinyl esters, such as vinyl acetate, maleimides, such as N-4-chlorophenyl maleimide and N-cyclohexyl maleimide, unsaturated adds, such as methacrylic add. Preferred are the lower alkyl, i.e. (C_1 to C_4)-alkyl acrylates, wherein lower alkyl refers to 1 to 4 carbon atoms, for reasons of good clarity, good ultraviolet stability, and enhancement of thermal stability of the resultant polymer. Especially preferred is the use of from about 1 to about 10 weight percent of an alkyl ester of acrylic acid with a C_1 to C_4 primary alcohol.

The polymer derived from units mainly of alkyl methacrylate esters may be further reacted under conditions which introduce cyclic glutarimide or glutaric anhydride groups, and then stabilized against degradation by sterilizing radiation with alcohols similar to those effective with the polymers of the alkyl methacrylates.

By the term "alcohol containing up to 10 carbon atoms" is meant an aliphatic compound, containing one or more hydroxyl groups, of from 1 to 10 carbon atoms. Examples of such alcohols include monohydric alkyl alcohols, such as methanol, ethanol, n-propanol, i-propanol, s-butanol, t-butanol and 2-ethylhexanol; polyhydric alkyl alcohols, such as ethylene glycol, glycerine, trimethylolpropane and pentaerythritol; and hydroxyesters, such as 2-hydroxyethyl acetate, diethylene glycol monoacetate and butyl lactate.

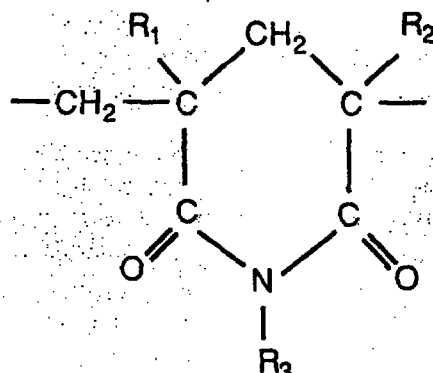
If the polymer during processing is to receive relatively little exposure to high heat, such as in casting and thermoforming a sheet, then the alcohol may be relatively volatile, such as methanol or ethanol. If the polymer is to be exposed to higher temperatures, such as polymerization at temperatures well above 100 degrees C, to devolatilization at such temperatures under vacuum or autonomous pressure, such as devolatilization of a monomer-polymer syrup or of a solution of polymer and monomer in a high-boiling solvent, or to high temperatures of processing, such as extrusion, then the alcohol should be high enough boiling so as not to be driven out during the processing steps. Alternatively, the alcohol may be added late in the sequence of processing steps, such as just prior to extrusion or molding of the final article.

For some uses where the resulting polymer will be exposed to sterilizing radiation, the polymer may be in the form of a sheet formed by "casting", which is bulk polymerization of the monomers between glass or metal surfaces, followed by optional thermoforming of the resulting sheet. For these purposes, the molecular weight of the polymer needs be above a minimum value where embrittlement may set in, such as about 20,000 weight-average molecular weight. Such cell-casting is a useful means for forming sheets later processed into useful objects, such as covers, viewing ports, containers, and the like, by thermoforming.

Especially useful in processes where molding is not utilized are cell-casting methods where essentially no residual monomer remains, which can be achieved by appropriate selection of initiators and polymerization times and temperatures.

Analogous to cell-casting methods are methods wherein the polymerization is conducted in bulk, such as in poly(vinyl alcohol) bags, and the polymer processed in an extruder to form molding pellets. Any residual monomer may be removed by devolatilization during such pelletization, and alcohol may be added at that time, along with other additives.

Further, imidized derivatives of poly(alkyl methacrylates), especially poly(methyl methacrylate), may also be protected against yellowing by sterilizing radiation by the addition of the alcohols of the present invention. By "imidized" is meant the polymer formed when an poly(alkyl methacrylate) is reacted with ammonia or an alkyl amine under pressure in an extruder to introduce cyclic units of the formula



where R¹ and or R² are CH₃ and R³ is H or alkyl. Such thermally stable polymers and their preparation are disclosed in US-A-4,246,374. Such polymers, which often also contain cyclic anhydride and free acid groups, may be further treated with alkylating agents to remove acid and anhydride functionality, as taught in US-A-4,727,117. Imidized polymers may be prepared by other methods known in the literature, as long as they meet the thermal stability criteria of Kopchik. The molecular weight of the polymer containing glutarimide units is preferably from 100,000 to 500,000, but polymers outside this molecular weight range stabilized with aliphatic alcohols may be useful in certain applications requiring sterilization.

As the imidized polymers undergo high temperatures and devolatilization during their preparation, it is preferable to add the alcohols and other additives to the melt after cyclization and alkylation have been completed. The alcohols to be added are those useful in combination with the poly(alkyl methacrylates) and are employed at similar levels.

The polymers containing glutarimide units will exhibit a higher service temperature than the (meth)acrylate polymers from which they are derived, and may be molded into useful objects, especially for use at high service temperature, such as lamp covers, automotive headlight covers, glazing, and the like. They may be molded into objects which require sterilization in a manner similar to the methacrylic polymers taught above. They are especially useful where heating and sterilization are required.

In a similar manner, units derived from glutaric anhydride may be incorporated into the polymer by methods known to the art, especially by treating the poly(alkyl methacrylate) with dimethyl amine in an extruder, as taught in US-A-4,874,824. Care must be taken in admixing the stabilizing alcohol that reaction does not occur with the anhydride ring.

For most purposes, the polymer will be shaped into a form which may be best achieved by injection-molding. In that case, the polymer molecular weight should not be excessive. A useful range is from about 20,000 to about 300,000, but a preferred range is from about 80,000 to about 150,000. Such molecular weight control may be achieved by control of the polymerization conditions, especially by the use of chain transfer agents. Use of an alkyl mercaptan, such as n-dodecyl mercaptan, at levels from about 0.01 to 0.5 weight percent, is preferred. Presence of the mercaptan, which during polymerization is chemically combined into the polymer in the form of a terminal sulfide group, is not detrimental to the stabilizing effect of the alcohol.

Polymers useful in this application may be prepared by many means other than cell- or bulk-casting. Such methods include suspension, emulsion, solution, and continuous bulk polymerization.

For many of the envisioned medical or other sterilizable uses, the toughness of the methacrylate polymer may not be sufficient. Known impact modifiers for methacrylate polymers may be added, such as polyurethane rubbers, graft polymers of methyl methacrylate or styrene/acrylonitrile to ethylene-propylene or ethylene-propylene-diene terpolymers, graft polymers of methyl methacrylate or methyl methacrylate/styrene or styrene/acrylonitrile onto butadiene-based rubbers, such as poly(butadiene) or butadiene-styrene or butadiene-acrylonitrile copolymers, or staged copolymers of styrene-acrylonitrile or of methyl methacrylate polymers onto a first stage of a alkyl acrylate or alkyl acrylate/styrene polymer. Most of these impact modifiers will be discolored and/or will suffer chemical changes as the result of exposure to sterilizing radiation, even when surrounded by the poly(methacrylate) matrix. For this reason, preferred for

uses requiring exposure to sterilizing radiation are those impact modifiers containing almost exclusively units derived from alkyl esters of methacrylic and acrylic acids. More preferred, as the main uses for such sterilized articles requires transparency, are those impact modifiers designed to retain the clarity of the poly(methacrylate) matrix, accomplished by control of refractive index and particle size of the various impact modifier components, such as by matching the refractive index of all components of the multistage polymer to that of the matrix polymer. Especially preferred for avoidance of discoloration during processing or exposure to various forms of radiation are those polymers based on a first stage of butyl acrylate copolymerized with styrene, optionally containing multifunctional monomers, such as glycol esters of acrylic or methacrylic acid, diallyl esters of maleic acid, allyl esters of methacrylic or acrylic acid, and the like, and a final stage of methyl methacrylate. Also especially preferred are those polymers having a hard core of a poly(alkyl methacrylate), an intermediate stage of butyl acrylate copolymerized with styrene, optionally containing multifunctional monomers, such as glycol esters of acrylic or methacrylic acid, diallyl esters of maleic acid, allyl esters of methacrylic or acrylic acid, and the like, and a final stage of methyl methacrylate.

The impact modifier may be blended in the molten state with the polymer of the alkyl methacrylate, or, if prepared in emulsion, may be admixed in emulsion form and co-coagulated, such as in a kettle or in an extruder. Further, the impact modifier may be added to a molten mixture of polymer and residual monomer, and the residual monomer concurrently devolatilized. The alcohol may be added at various stages of these processes, depending on its boiling point, and the temperatures, pressures, and times encountered.

The polymer may also contain conventional low levels of lubricants, such as stearyl alcohol, stearic acid, butyl stearate, and the like. It should be noted that stearyl alcohol, which is not a C_1 to C_{10} alkyl alcohol, is not effective in promoting resistance to color formation by sterilizing radiation. Other ultraviolet stabilizers may also be present, but if present, testing must be conducted to show that they do not cause discoloration on exposure to sterilizing radiation. Since the alcohols are effective ultraviolet stabilizers, it is generally not necessary to add a second ultraviolet stabilizer.

The polymers containing the stabilizers made by converted into useful objects by a variety of methods including molding, injection blow molding, extrusion blow-molding, calendering, thermoforming, profile extrusion, sheet extrusion, vacuum-assisted thermoforming, and the like. For many uses, especially in medical devices, injection molding is the method of choice. As the low level of alcohol has little effect on the rheological and other processing characteristics of the polymer, conventional means and techniques for processing the alkyl methacrylate polymer may be employed.

Sterilization of the formed objects may be accomplished by exposure to various forms of irradiation. Most often used are beta- and gamma-sources. The beta source delivers electrons to the object, and of several commercially available sources may be used. Most doses are delivered rapidly with concurrent heat build-up, so gamma radiation, which is slower and where the temperature of the object may be better controlled, is preferred. Gamma rays arise from decay of materials such as cobalt-60, and exposure to such sources may be achieved in a air, water, or nitrogen atmosphere. Doses are controlled by the time of exposure.

In the following Examples, which are given for the purposes of illustration only, measurement of the effect on color is conducted by means well known to the art. The total light transmittance and haze (ASTM D-1003) may be measured to quantify the retention of clarity. Standard means for measuring and reporting yellowness index changes (ASTM D-1005) measures the color changes which occur, even if transmittance is less stringently effected.

EXAMPLE 1

This example describes the preparative means for copolymers of methyl methacrylate/ethyl acrylate to be subjected to sterilizing radiation. In these mixtures, the mercaptan present in the mix was incorporated into the polymer chain; it was present to control and lower the molecular weight so that the resultant polymer can be injection molded. The C16-C18 alcohols were present as release agents when the polymer was injection molded.

In process A, a mixture of 94 parts methyl methacrylate (MMA), 5 parts ethyl acrylate (EA), 0.472 parts n-dodecylmercaptan (n-DDM), 0.5 parts of a cetyl-stearyl alcohol (C16- C18 mixture), .01 parts of azo-(bisobutyronitrile)(AIBN), .01 parts of t-butyl peroxyvalerate, .01 parts of t-butyl peroxyacetate, and the selected amount of stabilizing alcohol were mixed. The mixture was degassed, charged to poly(vinyl alcohol) bags, and polymerized in an oven at 60 degrees C until any exotherm has subsided, then at 80 degrees C for four hours, and then at 120 degrees C for at least four hours. The bags were stripped from the polymer, the polymer broken into small pieces, and fed to an extruder equipped with a strand die and strand cutter to prepare pellets for molding. Pellets were molded in a ASTM molds under conditions

recommended for commercial acrylic molding powders into test bars of 3.18 mm. thickness. For a reciprocating screw machine, samples would be dried at 87 degrees C. to remove any water, and processed at a melt temperature ca. 230 degrees C., and a mold temperature of ca. 65 degrees C.

In process B, a higher molecular weight cast sheet was prepared. A mixture of MMA 96, EA 4, AIBN 0.0075, and the alcohol was degassed, charged between glass plates separated by a 4.75 mm. vinyl spacer, the gasket seal closed, and the mixture heated at 66 degrees C. overnight, followed by polymerization "finish-off" similar to process A. The plate glass was removed to yield a casting for irradiation.

In process C, a polymer of MMA/EA ca. 95.5/4.5 obtained as a commercial molding resin free from any ultraviolet stabilizer was processed in a twin screw extruder and a mixture of 1 part butyl lactate in 2 parts ethanol was added to the melt. The melt was stranded, cut into pellets, and remolded as in process A; in this case both 3.18 (Example 11) and 4.75 mm. (Ex. 12) thick bars were obtained for irradiation.

EXAMPLES 2-12

In these examples are described the actual formulations studied (Table I) and the results of exposure to a targeted exposure of three Megarads (actual dosage 2.84 to 2.98 Megarads) of gamma irradiation at a commercial source of unknown configuration (Table II). The optical methods for measurement are described earlier. Parts of alcohol are in addition to the parts of monomer, etc. described in Example 1. EG is ethylene glycol, BL is butyl lactate. Certain examples (4, 7, 10) contain higher levels of alcohol, and are plasticized by that level so as to lower service temperature and modulus, although imparting an even higher degree of stabilization to sterilizing radiation. In all cases shown, the low level of alcohol used produces a very significant advantage in resistance to yellowing.

TABLE I

Formulations Containing Alcohol				
Example	Polymer from Process	Alcohol I, parts	Alcohol II, parts	Other alcohols
2	A (control)	---	---	---
3	A	EG, 1	glycerine, 1	t-butanol, 5; BL 5.
4	A (excess)	EG, 1	glycerine, 1	
5	B (control)	---	---	
6	B	methanol, 2	---	
7	B (excess)	methanol, 5	---	---
8	B	ethanol, 2	---	---
9	B	i-propanol, 2	---	---
10	B(excess)	i-propanol, 5	---	---
11	C	ethanol, 2	BL, 1	
12	C	ethanol, 2	BL, 1	

Table 2

Optical Property Data After Exposure to 3 Mrad Gamma Radiation							
Sample ID	Thick	% Transmission		D % Transmission		YI	YI
		300nm	340nm	300nm	340nm		
Ex.2 (Control)	0.120 *	49.8	77.7	-	-	+1.6	-
	0.121	0.5	27.3	-49.3	-50.4	+11.1	+9.6
	0.120	0.6	27.6	-49.2	-50.1	+11.0	+9.4
	0.120	0.6	27.8	-49.2	-49.9	+10.9	+9.3
Ex. 3	0.125 *	56.0	78.8	-	-	+2.0	-
	0.125	26.8	69.6	-29.2	-9.2	+3.1	+1.0
	0.125	26.8	69.4	-29.2	-9.4	+3.0	+1.0
	0.125	27.5	69.7	-28.5	-9.1	+3.0	+1.0
Ex. 4 (Excess)	0.123*	59.1	83.2	-	-	+1.4	-
	0.123	54.4	80.9	-4.7	-2.3	+1.5	+0.1
	0.123	55.0	81.1	-4.1	-2.1	+1.5	+0.1
	0.123	54.8	80.8	-4.3	-2.4	+1.5	+0.1
Ex. 5 (Control)	0.187*	80.0	89.5	-	-	+0.7	-
	0.187	0.4	13.7	-79.6	-75.8	+14.9	+14.2
Ex. 6	0.187*	84.6	89.8	-	-	+0.8	-
	0.187	36.3	78.1	-48.3	-11.7	+1.7	+0.9
Ex. 7 (Excess)	0.187*	82.9	90.0	-	-	+0.8	-
	0.187	61.6	86.8	-21.3	-3.2	+0.6	-0.2
Ex. 8	0.187*	83.6	89.5	-	-	+0.9	-
	0.187	39.9	77.9	-43.7	-11.6	+1.5	+0.6
Ex. 9	0.187*	84.2	89.2	-	-	+0.9	-
	0.187	20.3	65.9	-63.9	-23.3	+2.8	+1.9
Ex. 10 (Excess)	0.187*	82.6	89.8	-	-	+0.9	-
	0.187	53.6	86	-29.0	-3.8	+0.9	0
Ex. 11	0.125*	79.6	87.3	-	-	+0.8	-
	0.125	27.8	70.8	-51.8	-16.5	+2.4	+1.6
Ex. 12	0.187*	69.4	84.8	-	-	+1.0	-
	0.187	13.4	60.4	-56.0	-24.4	+3.4	+2.4

* - not exposed to radiation

EXAMPLE 13

An impact modifier of the composition of Example 8 of US-A-3,793,402, was prepared in emulsion by the method taught in that patent, was isolated by spray-drying, and was blended with a equivalent amount of poly(methyl methacrylate) molding powder of MW ca. 110,000 as taught in Example 1 of US-A-3793402. No UV stabilizer was present. The blend was prepared on a single screw Killion extruder of 38.1 mm. diameter. at a melt temperature of 218 degrees C.

To the blend was added in the melt stage various levels (0.5, 1, and 2.5 wt. %) of butyl lactate. Extrusion was conducted for a long enough time to purge any overlap of samples. Prior to the addition of the butyl lactate, enough polymer blend free of alcohol was extruded to serve as a control. The samples were molded into test pieces as in Example 1, but at a melt temperature of 220 degrees C. and a mold temperature of 76 degrees C. These are conditions similar to those recommended for commercial impact-modified acrylic plastics.

Exposure to ca. 3 MRads of gamma irradiation, as in Example 1, demonstrated less color formation and better retention of transmission of UV and visible light for the samples containing the butyl lactate.

EXAMPLE 14

A mixture of methyl methacrylate 95.26, ethyl acrylate 4.5, and n-dodecyl mercaptan 0.22% was polymerized in a continuous flow, stirred tank reactor with an organic peroxide to ca. 50% conversion, the polymer-monomer mixture pumped to a devolatilizing twin-screw extruder where residual monomer was removed, and then various levels of butyl lactate (BL) admixed with the molten polymer. Samples were prepared with 0%(control), 1%, 2%, and 5% BL. The polymers were stabilized were conveyed by the extruder to an extruding die, and the polymers stranded and cut into pellets. Materials were molded for exposure to sterilizing irradiation and physical testing as in Example 1. Exposure to ca. 3 MRads of gamma irradiation, as in Example 1, demonstrated less color formation and better retention of transmission of UV and visible light for the samples containing the butyl lactate.

EXAMPLES 15 - 20

These examples illustrate formulations of a polyglutarimide stabilized against sterilizing radiation by aliphatic hydroxy compounds. A poly(methyl methacrylate) of molecular weight ca. 150,000 is treated with methylamine in an extruder and then post-treated to reduce the content of acid and anhydride groups in a manner similar to Example 32 of US-A-4,727,117. The Vicat softening temperature of the resultant polymer is ca. 145 degrees C. One preparation contains no stabilizer; a second preparation contains 0.15 weight percent of tris(nonylphenyl phosphite) and 0.25 weight percent of a commercial ultraviolet stabilizer, 2-(2-hydroxy-5-t-octylphenyl)benzotriazole, added after the post-treatment but prior to stranding and pelletizing.

The pellets of polymer are blended with either ethylene glycol or butyl lactate (1.2 weight percent on polymer), and then re-extruded in a single screw extruder at a set temperature of 232 degrees C., and the pellets are molded into appropriate test pieces at a melt temperature of 280 degrees C. and a mold temperature of 104 degrees C. The control with no additives is molded directly from pellets, and so has received less thermal history. The test pieces are exposed to gamma radiation as in Example 1.

Example	Weight Percent		EG	BL
	TNPP	C-5411		
15	0.15	0.25	---	---
16	0.15	0.25	1.2	---
17	0.15	0.25	---	1.2
18	---	---	1.2	---
19	---	---	---	1.2
20	---	---	---	---
TNPP is tris(nonylphenyl)phosphite; C-5411 is 2-(2-hydroxy-5-t-octylphenyl)benzotriazole; EG is ethylene glycol; BL is butyl lactate.				

Claims

1. The use of non-polymerisable aliphatic alcohol containing up to ten carbon atoms, in the absence of other ultraviolet stabiliser, to impart resistance to sterilising radiation to polymer comprising at least 50% by weight units of (C₁-C₄)-alkyl esters, cyclohexyl ester or isobornyl ester of methacrylic acid and/or N-hydrogen or N-alkyl dimethylglutarimide, and, optionally, other vinyl or vinylidene monomer units said alcohol being used in an amount of 0.5 to 2% by weight based on the weight of said polymer.
2. Use as claimed in Claim 1 wherein the polymer is present in admixture with a core/shell impact modifier, and wherein the core comprises predominantly (C₁-C₄)-alkyl acrylate units.

Exposure to ca. 3 MRads of gamma irradiation, as in Example 1, demonstrated less color formation and better retention of transmission of UV and visible light for the samples containing the butyl lactate.

EXAMPLE 14

A mixture of methyl methacrylate 95.26, ethyl acrylate 4.5, and n-dodecyl mercaptan 0.22% was polymerized in a continuous flow, stirred tank reactor with an organic peroxide to ca. 50% conversion, the polymer-monomer mixture pumped to a devolatilizing twin-screw extruder where residual monomer was removed, and then various levels of butyl lactate (BL) admixed with the molten polymer. Samples were prepared with 0%(control), 1%, 2%, and 5% BL. The polymers were stabilized were conveyed by the extruder to an extruding die, and the polymers stranded and cut into pellets. Materials were molded for exposure to sterilizing irradiation and physical testing as in Example 1. Exposure to ca. 3 MRads of gamma irradiation, as in Example 1, demonstrated less color formation and better retention of transmission of UV and visible light for the samples containing the butyl lactate.

EXAMPLES 15 - 20

These examples illustrate formulations of a polyglutarimide stabilized against sterilizing radiation by aliphatic hydroxy compounds. A poly(methyl methacrylate) of molecular weight ca. 150,000 is treated with methylamine in an extruder and then post-treated to reduce the content of acid and anhydride groups in a manner similar to Example 32 of US-A-4,727,117. The Vicat softening temperature of the resultant polymer is ca. 145 degrees C. One preparation contains no stabilizer; a second preparation contains 0.15 weight percent of tris(nonylphenyl phosphite) and 0.25 weight percent of a commercial ultraviolet stabilizer, 2-(2-hydroxy-5-t-octylphenyl)benzotriazole, added after the post-treatment but prior to stranding and pelletizing.

The pellets of polymer are blended with either ethylene glycol or butyl lactate (1.2 weight percent on polymer), and then re-extruded in a single screw extruder at a set temperature of 232 degrees C., and the pellets are molded into appropriate test pieces at a melt temperature of 280 degrees C. and a mold temperature of 104 degrees C. The control with no additives is molded directly from pellets, and so has received less thermal history. The test pieces are exposed to gamma radiation as in Example 1.

Example	Weight Percent		EG	BL
	TNPP	C-5411		
15	0.15	0.25	---	---
16	0.15	0.25	1.2	---
17	0.15	0.25	---	1.2
18	---	---	1.2	---
19	---	---	---	1.2
20	---	---	---	---

TNPP is tris(nonylphenyl)phosphite; C-5411 is 2-(2-hydroxy-5-t-octylphenyl)benzotriazole; EG is ethylene glycol; BL is butyl lactate.

Claims

1. The use of non-polymerisable aliphatic alcohol containing up to ten carbon atoms, in the absence of other ultraviolet stabiliser, to impart resistance to sterilising radiation to polymer comprising at least 50% by weight units of (C₁-C₄)-alkyl esters, cyclohexyl ester or isobornyl ester of methacrylic acid and/or N-hydrogen or N-alkyl dimethylglutarimide, and, optionally, other vinyl or vinylidene monomer units said alcohol being used in an amount of 0.5 to 2% by weight based on the weight of said polymer.
2. Use as claimed in Claim 1 wherein the polymer is present in admixture with a core/shell impact modifier, and wherein the core comprises predominantly (C₁-C₄)-alkyl acrylate units.



3. Use as claimed in Claim 2 wherein the impact modifier comprises three stages in the sequence hard/soft/hard wherein the hard stages have a Tg of at least 20 °C (preferably at least 70 °C) and comprise (C₁-C₄)-alkyl methacrylate, preferably methyl methacrylate, units, and the soft stage has a Tg of less than 20 °C and comprises (C₁-C₄)-alkyl acrylate, preferably butylacrylate, units, the first hard stage and/or the soft stage optionally also containing units of vinyl aromatic monomer.
4. Use as claimed in any preceding Claim in polymer composition in the form of a container, tube, medical tool or other shaped article.
5. Use as claimed in any preceding Claim wherein the alcohol comprises methyl alcohol, ethyl alcohol, ethylene glycol, diethylene glycol, glycerine or butyl lactate.
6. Use as claimed in any preceding Claim wherein the polymer has a weight average molecular weight of from 100,000 to 500,000.
7. Use as claimed in any preceding Claim wherein the polymer comprises units of methyl methacrylate, and/or N-methyl dimethylglutarimide.

Patentansprüche

1. Verwendung eines nicht-polymerisierbaren aliphatischen Alkohols, der bis zu zehn Kohlenstoffatome enthält, um einem Polymer in Abwesenheit eines anderen Ultraviolettstabilisators Beständigkeit gegen sterilisierende Strahlung zu verleihen, welches Polymer mindestens 50 Gew.-% Einheiten von (C₁ bis C₄)-Alkylester, Cyclohexylester oder Isobornylester der Methacrylsäure und/oder N-Wasserstoff- oder N-Alkyldimethylglutarimid und gegebenenfalls andere Vinyl- oder Vinylidenmonomereinheiten umfaßt, wobei der Alkohol in einer Menge von 0,5 bis 2 Gew.-%, bezogen auf das Gewicht des Polymers, verwendet wird.
2. Verwendung, wie in Anspruch 1 beansprucht, wobei das Polymer in einem Gemisch mit einem Kern/Hülle-Schlagfestigkeitsmodifikator vorhanden ist, und wobei der Kern vorwiegend (C₁-C₄)-Alkylacrylateinheiten umfaßt.
3. Verwendung, wie in Anspruch 2 beansprucht, wobei der Schlagfestigkeitsmodifikator drei Stufen in der Sequenz hart/weich/hart umfaßt, wobei die harten Stufen eine Tg von mindestens 20 °C (vorzugsweise mindestens 70 °C) besitzen und (C₁-C₄)-Alkylmethacrylateinheiten, vorzugsweise Methylmethacrylateinheiten, umfassen und die weiche Stufe eine Tg von weniger als 20 °C aufweist und (C₁-C₄)-Alkylacrylateinheiten, vorzugsweise Butylacrylateinheiten, umfaßt, wobei die erste harte Stufe und/oder die weiche Stufe gegebenenfalls auch Einheiten eines vinylaromatischen Monomers enthält.
4. Verwendung, wie in einem vorhergehenden Anspruch beansprucht, in einer Polymerzusammensetzung in der Form eines Behälters, eines Rohrs, eines medizinischen Instruments oder eines anderen geformten Gegenstandes.
5. Verwendung, wie in einem vorhergehenden Anspruch beansprucht, wobei der Alkohol Methylalkohol, Ethylalkohol, Ethylenglycol, Diethylenglycol, Glycerin oder Butylactat umfaßt.
6. Verwendung, wie in einem vorhergehenden Anspruch beansprucht, wobei das Polymer ein Gewichtsmittel des Molekulargewichts von 100.000 bis 500.000 aufweist.
7. Verwendung, wie in einem vorhergehenden Anspruch beansprucht, wobei das Polymer Einheiten von Methylmethacrylat und/oder N-Methyldimethylglutarimid umfaßt.

Revendications

1. Utilisation d'un alcool aliphatique non polymérisable contenant jusqu'à 10 atomes de carbone, en l'absence d'un autre stabilisant UV, pour conférer une résistance aux rayonnements stérilisants à un polymère constitué d'au moins 50 % en poids de motifs d'esters alkyls en C₁-C₄, de l'ester cyclohexylique ou de l'ester isobornylique de l'acide méthacrylique et/ou de N-hydrogène ou de N-



alkyldiméthylglutarimide, et éventuellement d'autres motifs monomères vinyliques ou vinyldéniques, cet alcool étant utilisé en une quantité de 0,5 à 2 % en poids par rapport au poids dudit polymère.

2. Utilisation selon la revendication 1, dans laquelle le polymère est présent en mélange avec un agent modifiant de choc de type coeur/enveloppe, et dans laquelle le coeur comprend essentiellement des motifs d'un acrylate d'alkyle en C₁-C₄.
3. Utilisation selon la revendication 2, dans laquelle l'agent modifiant de choc comprend trois étages, dans l'ordre dur/souple/dur, où les étages durs ont une Tg d'au moins 20 °C (de préférence d'au moins 70 °C) et comprennent des motifs d'un méthacrylate d'alkyle en C₁-C₄, de préférence de méthacrylate de méthyle, et l'étage souple a une Tg inférieure à 20 °C et comprend des motifs d'un acrylate d'alkyle en C₁-C₄, de préférence d'acrylate de butyle, le premier étage dur et/ou l'étage souple contenant aussi, éventuellement, des motifs d'un monomère vinylaromatique.
4. Utilisation selon l'une quelconque des revendications précédentes, dans une composition polymère sous forme d'un récipient, d'un tube, d'un instrument médical ou d'un autre article façonné.
5. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle l'alcool comprend l'alcool méthylique, l'alcool éthylique, l'éthylèneglycol, le diéthylèneglycol, le glycérol ou le lactate de butyle.
6. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le polymère a une masse moléculaire moyenne en masse de 100 000 à 500 000.
7. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le polymère comprend des motifs de méthacrylate de méthyle et/ou de N-méthylidiméthylglutarimide.

