Title: THERMOPLASTIC POLYCARBONATE COMPOSITIONS, METHODS OF MANUFACTURE, AND METHOD OF USE THEREOF

Abstract: A thermoplastic compositions comprising in combination a polycarbonate component; and an impact modifier comprising wherein the components of the impact modifier composition are substantially free of a species that degrades a polycarbonate, the components comprising a bulk polymerized ABS; and an impact modifier different from the ABS. The compositions have significantly increased hydrolytic stability, in combination with good thermal stability and/or impact strength.
THERMOPLASTIC POLYCARBONATE COMPOSITIONS, METHOD OF MANUFACTURE, AND METHOD OF USE THEREOF

BACKGROUND

This invention is directed to thermoplastic compositions comprising aromatic polycarbonate, their method of manufacture, and method of use thereof, and in particular impact-modified thermoplastic polycarbonate compositions having improved stability.

Aromatic polycarbonates are useful in the manufacture of articles and components for a wide range of applications, from automotive parts to electronic appliances. Impact modifiers are commonly added to aromatic polycarbonates to improve the toughness of the compositions. The impact modifiers often have a relatively rigid thermoplastic phase and an elastomeric (rubbery) phase, and may be formed by bulk or emulsion polymerization. Polycarbonate compositions comprising acrylonitrile-butadiene-styrene (ABS) impact modifiers are described generally, for example, in U.S. Patent No. 3,130,177 and U.S. Patent No. 3,130,177. Polycarbonate compositions comprising emulsion polymerized ABS impact modifiers are described in particular in U.S. Publication No. 2003/0119986. U.S. Publication No. 2003/0092837 discloses use of a combination of a bulk polymerized ABS and an emulsion polymerized ABS.

Of course, a wide variety of other types of impact modifiers for use in polycarbonate compositions have also been described. While suitable for their intended purpose of improving toughness, many impact modifiers may also adversely affect other properties, such as processability, hydrolytic stability, and/or low temperature impact strength, particularly upon prolonged exposure to high humidity and/or high temperature such as may be found in Southeast Asia. Thermal aging stability of polycarbonate compositions, in particular, is often degraded with the addition of rubbery impact modifiers. There remains a continuing need in the art, therefore, for impact-modified thermoplastic polycarbonate compositions having a combination of good properties, including toughness and hydrolytic stability. It would further be
advantageous if hydrolytic stability could be improved without significantly adversely affecting other desirable properties of polycarbonates.

SUMMARY OF THE INVENTION

In one embodiment, a thermoplastic composition comprises in combination in combination a polycarbonate component; and an impact modifier composition wherein the components of the impact modifier composition are substantially free of a species that degrades a polycarbonate, the components comprising a bulk polymerized ABS; and an impact modifier different from the ABS.

In another embodiment, an article comprises the above thermoplastic composition.

In still another embodiment, a method of manufacture of an article comprises molding, extruding, or shaping the above thermoplastic composition.

In still another embodiment, a method for the manufacture of a thermoplastic composition having improved hydrolytic and/or thermal stability, the method comprising admixture of a polycarbonate, a bulk polymerized ABS, and an impact modifier different from the ABS, wherein each component of the composition is essentially free from a species that degrades the polycarbonate.

DETAILED DESCRIPTION OF THE INVENTION

It has been discovered by the inventors hereof that use of a combination of specific impact modifiers provides greatly improved hydrolytic stability to thermoplastic compositions containing polycarbonate, while at the same time maintaining their thermal stability and/or impact resistance. The improvement in hydrolytic stability without significantly adversely affecting thermal stability is particularly unexpected, as the thermal stability of similar compositions can be significantly worse. It has further been discovered that an advantageous combination of other physical properties, in addition to good hydrolytic stability, can be obtained by use of the specific combination of impact modifiers.
As used herein, the terms “polycarbonate” and “polycarbonate resin” means compositions having repeating structural carbonate units of formula (1):

\[
\begin{array}{c}
\text{O} \\
\hline
\text{R}^1 \text{--O--C--O--}
\end{array} 
\]  

(1)

in which at least about 60 percent of the total number of \( R^1 \) groups are aromatic organic radicals and the balance thereof are aliphatic, alicyclic, or aromatic radicals. In one embodiment each \( R^1 \) is an aromatic organic radical and, more specifically, a radical of formula (2):

\[
\begin{array}{c}
\text{A}^1 \\
\hline
\text{Y}^1 \\
\text{A}^2
\end{array} 
\]  

(2)

wherein each of \( A^1 \) and \( A^2 \) is a monocyclic divalent aryl radical and \( Y^1 \) is a bridging radical having one or two atoms that separate \( A^1 \) from \( A^2 \). In an exemplary embodiment, one atom separates \( A^1 \) from \( A^2 \). Illustrative non-limiting examples of radicals of this type are -O-, -S-, -S(O)-, -S(O)2-, -C(O)-, methylene, cyclohexylmethylene, 2-[2.2.1]-bicycloheptylidene, ethylidene, isopropylidene, neopentylidene, cyclohexylidene, cyclopentadecylidene, cyclododecylidene, and adamantylidene. The bridging radical \( Y^1 \) may be a hydrocarbon group or a saturated hydrocarbon group such as methylene, cyclohexylidene, or isopropylidene.

Polycarbonates may be produced by the interfacial reaction of dihydroxy compounds having the formula \( \text{HO-R}^1\text{--OH} \), which includes dihydroxy compounds of formula (3)

\[
\begin{array}{c}
\text{HO} \\
\hline
\text{A}^1 \\
\text{Y}^1 \\
\text{A}^2 \text{--OH}
\end{array} 
\]  

(3)

wherein \( Y^1 \), \( A^1 \) and \( A^2 \) are as described above. Also included are bisphenol compounds of general formula (4):

\[
\begin{array}{c}
\text{HO} \quad (R^2)_p \\
\hline
X^a \\
(R^5)_q \\
\text{OH}
\end{array} 
\]  

(4)
wherein R<sup>a</sup> and R<sup>b</sup> each represent a halogen atom or a monovalent hydrocarbon group and may be the same or different; p and q are each independently integers of 0 to 4; and X<sup>e</sup> represents one of the groups of formula (5):

\[
\begin{align*}
\text{R}^e \quad \text{C} & \quad \text{or} \quad \text{R}^e \\
\text{R}^d
\end{align*}
\]

(5)

wherein R<sup>e</sup> and R<sup>d</sup> each independently represent a hydrogen atom or a monovalent linear or cyclic hydrocarbon group and R<sup>e</sup> is a divalent hydrocarbon group.

Some illustrative, non-limiting examples of suitable dihydroxy compounds include the following: resorcinol, 4-bromoresorcinol, hydroquinone, 4,4'-dihydroxybiphenyl, 1,6-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)diphenylmethane, bis(4-hydroxyphenyl)-1-naphthylmethane, 1,2-bis(4-hydroxyphenyl)ethane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, 2-(4-hydroxyphenyl)-2-(3-hydroxyphenyl)propane, bis(4-hydroxyphenyl)phenylmethane, 2,2-bis(4-hydroxy-3-bromophenyl)propane, 1,1-bis(hydroxyphenyl)cyclopentane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 1,1-bis(4-hydroxyphenyl)isobutene, 1,1-bis(4-hydroxyphenyl)cyclododecane, trans-2,3-bis(4-hydroxyphenyl)-2-butene, 2,2-bis(4-hydroxyphenyl)adamantine, (alpha, alpha'-bis(4-hydroxyphenyl)toluene, bis(4-hydroxyphenyl)acetonitrile, 2,2-bis(3-methyl-4-hydroxyphenyl)propane, 2,2-bis(3-ethyl-4-hydroxyphenyl)propane, 2,2-bis(3-n-propyl-4-hydroxyphenyl)propane, 2,2-bis(3-isopropyl-4-hydroxyphenyl)propane, 2,2-bis(3-sec-butyl-4-hydroxyphenyl)propane, 2,2-bis(3-t-butyl-4-hydroxyphenyl)propane, 2,2-bis(3-cyclohexyl-4-hydroxyphenyl)propane, 2,2-bis(3-allyl-4-hydroxyphenyl)propane, 2,2-bis(3-methoxy-4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)hexafluoropropane, 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene, 1,1-dibromo-2,2-bis(4-hydroxyphenyl)ethylene, 1,1-dichloro-2,2-bis(5-phenoxy-4-hydroxyphenyl)ethylene, 4,4'-dihydroxybenzophenone, 3,3-bis(4-hydroxyphenyl)-2-butane, 1,6-bis(4-hydroxyphenyl)-1,6-hexanediene, ethylene glycol bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)sulfite, bis(4-hydroxyphenyl)sulfone, 9,9-bis(4-
hydroxyphenyl)fluorine, 2,7-dihydroxyphycene, 6,6'-dihydroxy-3,3,3',3'-
tetramethylspiro(bis)indane ("spiropiindane bisphenol"), 3,3-bis(4-
hydroxyphenyl)phthalide, 2,6-dihydroxydibenzo-p-dioxin, 2,6-dihydroxythianthrene,
2,7-dihydroxyphenoxathin, 2,7-dihydroxy-9,10-dimethylphenazine, 3,6-
dihydroxydibenzofuran, 3,6-dihydroxydibenzothiophene, and 2,7-
dihydroxycarbazole, and the like. Combinations comprising at least one of the
foregoing dihydroxy compounds may also be used.

A nonexclusive list of specific examples of the types of bisphenol compounds that
may be represented by formula (3) includes 1,1-bis(4-hydroxyphenyl) methane, 1,1-
bis(4-hydroxyphenyl) ethane, 2,2-bis(4-hydroxyphenyl) propane (hereinafter
"bisphenol A" or "BPA"), 2,2-bis(4-hydroxyphenyl) butane, 2,2-bis(4-
hydroxyphenyl) octane, 1,1-bis(4-hydroxyphenyl) propane, 1,1-bis(4-hydroxyphenyl)
n-butane, 2,2-bis(4-hydroxy-1-methylphenyl) propane, and 1,1-bis(4-hydroxy-t-
butylphenyl) propane. Combinations comprising at least one of the foregoing
bisphenol compounds may also be used.

Branched polycarbonates are also useful, as well as blends comprising a linear
polycarbonate and a branched polycarbonate. The branched polycarbonates may be
prepared by adding a branching agent during polymerization, for example a
polyfunctional organic compound containing at least three functional groups
selected from hydroxyl, carboxyl, carboxylic anhydride, haloformyl, and mixtures of
the foregoing functional groups. Specific examples include trimellitic acid,
trimellitic anhydride, trimellitic trichloride, tris-p-hydroxyphenylethane, isatin-bis-
phenol, tris-phenol TC (1,3,5-tris((p-hydroxyphenyl)isopropyl)benzene), tris-phenol
PA (4(4(1,1-bis(p-hydroxyphenyl)-ethyl) alpha, alpha-dimethyl benzylphenol), 4-
chloroformyl phthalic anhydride, trimesic acid, and benzophenone tetracarboxylic
acid. The branching agents may be added at a level of about 0.05-2.0 wt.%. All
types of polycarbonate end groups are contemplated as being useful in the
polycarbonate composition, provided that such end groups do not significantly affect
desired properties of the thermoplastic compositions.
Suitable polycarbonates can be manufactured by processes such as interfacial polymerization and melt polymerization. Although the reaction conditions for interfacial polymerization may vary, an exemplary process generally involves dissolving or dispersing a dihydric phenol reactant in aqueous caustic soda or potash, adding the resulting mixture to a suitable water-immiscible solvent medium, and contacting the reactants with a carbonate precursor in the presence of a suitable catalyst such as triethylamine or a phase transfer catalyst, under controlled pH conditions, e.g., about 8 to about 10. The most commonly used water immiscible solvents include methylene chloride, 1,2-dichloroethane, chlorobenzene, toluene, and the like. Suitable carbonate precursors include, for example, a carbonyl halide such as carbonyl bromide or carbonyl chloride, or a haloformate such as a bishaloformates of a dihydric phenol (e.g., the bischloroformates of bisphenol A, hydroquinone, and the like) or a glycol (e.g., the bishaloformate of ethylene glycol, neopentyl glycol, polyethylene glycol, and the like). Combinations comprising at least one of the foregoing types of carbonate precursors may also be used.

Among the exemplary phase transfer catalysts that may be used are catalysts of the formula (R^3)_4Q^+X^-, wherein each R^3 is the same or different, and is a C_{1-10} alkyl group; Q is a nitrogen or phosphorus atom; and X is a halogen atom or a C_{1-8} alkoxy group or C_{6-188} aryloxy group. Suitable phase transfer catalysts include, for example, [CH_3(CH_2)_3]_4NX, [CH_3(CH_2)_3]_4PX, [CH_3(CH_2)_3]_4NX, [CH_3(CH_2)_3]_4NX, [CH_3(CH_2)_3]_4NX, [CH_3(CH_2)_3]_4NX, and CH_3[CH_3(CH_2)_3]_3NX wherein X is Cl, Br, a C_{1-8} alkoxy group or C_{6-188} aryloxy group. An effective amount of a phase transfer catalyst may be about 0.1 to about 10 wt.% based on the weight of bisphenol in the phosgenation mixture. In another embodiment an effective amount of phase transfer catalyst may be about 0.5 to about 2 wt.% based on the weight of bisphenol in the phosgenation mixture.

Alternatively, melt processes may be used. Generally, in the melt polymerization process, polycarbonates may be prepared by co-reacting, in a molten state, the dihydroxy reactant(s) and a diaryl carbonate ester, such as diphenyl carbonate, in the presence of a transesterification catalyst. Volatile monohydric phenol is removed.
from the molten reactants by distillation and the polymer is isolated as a molten residue.

In one specific embodiment, the polycarbonate is a linear homopolymer derived from bisphenol \( A \), in which each of \( A^1 \) and \( A^2 \) is p-phenylene and \( Y^1 \) is isopropylidene. The polycarbonates may have an intrinsic viscosity, as determined in chloroform at 25°C, of about 0.3 to about 1.5 deciliters per gram (dl/gm), specifically about 0.45 to about 1.0 dl/gm. The polycarbonates may have a weight average molecular weight of about 10,000 to about 200,000, specifically about 20,000 to about 100,000 as measured by gel permeation chromatography. The polycarbonates are substantially free of impurities, residual acids, residual bases, and/or residual metals that may catalyze the hydrolysis of polycarbonate.

"Polycarbonate" and "polycarbonate resin" as used herein further includes copolymers comprising carbonate chain units together with a different type of chain unit. Such copolymers may be random copolymers, block copolymers, dendrimers and the like. One specific type of copolymer that may be used is a polyester carbonate, also known as a copolyester-polycarbonate. Such copolymers further contain, in addition to recurring carbonate chain units of the formula (1), repeating units of formula (6)

\[
\begin{align*}
&\text{O} \quad \text{T} \quad \text{O} \\
&\text{C} \quad \text{T} \quad \text{C} \quad \text{O} \quad \text{E} \quad \text{O} 
\end{align*}
\]

wherein \( E \) is a divalent radical derived from a dihydroxy compound, and may be, for example, a \( C_{2-10} \) alkylene radical, a \( C_{6-20} \) alicyclic radical, a \( C_{6-20} \) aromatic radical or a polyoxyalkylene radical in which the alkylene groups contain 2 to about 6 carbon atoms, specifically 2, 3, or 4 carbon atoms; and \( T \) divalent radical derived from a dicarboxylic acid, and may be, for example, a \( C_{2-10} \) alkylene radical, a \( C_{6-20} \) alicyclic radical, a \( C_{6-20} \) alkyl aromatic radical, or a \( C_{6-20} \) aromatic radical.

In one embodiment, \( E \) is a \( C_{2-6} \) alkylene radical. In another embodiment, \( E \) is derived from an aromatic dihydroxy compound of formula (7):
wherein each $R^f$ is independently a halogen atom, a $C_{1-10}$ hydrocarbon group, or a $C_{1-10}$ halogen substituted hydrocarbon group, and $n$ is 0 to 4. The halogen is preferably bromine. Examples of compounds that may be represented by the formula (7) include resorcinol, substituted resorcinol compounds such as 5-methyl resorcinol, 5-ethyl resorcinol, 5-propyl resorcinol, 5-butyl resorcinol, 5-t-butyl resorcinol, 5-phenyl resorcinol, 5-cumyl resorcinol, 2,4,5,6-tetrafluororesorcinol, 2,4,5,6-tetrabromo resorcinol, and the like; catechol; hydroquinone; substituted hydroquinones such as 2-methyl hydroquinone, 2-ethyl hydroquinone, 2-propyl hydroquinone, 2-butyl hydroquinone, 2-t-butyl hydroquinone, 2-phenyl hydroquinone, 2-cumyl hydroquinone, 2,3,5,6-tetramethyl hydroquinone, 2,3,5,6-tetra-t-butyl hydroquinone, 2,3,5,6-tetrafluorohydroquinone, 2,3,5,6-tetrabromo hydroquinone, and the like; or combinations comprising at least one of the foregoing compounds.

Examples of aromatic dicarboxylic acids that may be used to prepare the polyesters include isophthalic or terephthalic acid, 1,2-di(p-carboxyphenyl)ethane, 4,4'-dicarboxydiphenyl ether, 4,4'-bisbenzoic acid, and mixtures comprising at least one of the foregoing acids. Acids containing fused rings can also be present, such as in 1,4-, 1,5-, or 2,6-naphthalenedicarboxylic acids. Specific dicarboxylic acids are terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, cyclohexane dicarboxylic acid, or mixtures thereof. A specific dicarboxylic acid comprises a mixture of isophthalic acid and terephthalic acid wherein the weight ratio of terephthalic acid to isophthalic acid is about 10:1 to about 0.2:9.8. In another specific embodiment, $E$ is a $C_{2-6}$ alkylene radical and $T$ is p-phenylene, m-phenylene, naphthalene, a divalent cycloaliphatic radical, or a mixture thereof. This class of polyester includes the poly(alkylene terephthalates).

The copolyester-polycarbonate resins are also prepared by interfacial polymerization. Rather than using the dicarboxylic acid per se, it is possible, and sometimes even preferred, to employ the reactive derivatives of the acid, such as the
corresponding acid halides, in particular the acid dichlorides and the acid dibromides. Thus, for example instead of using isophthalic acid, terephthalic acid, and mixtures thereof, it is possible to employ isophthaloyl dichloride, terephthaloyl dichloride, and mixtures thereof. The copolyester-poly carbonate resins may have an intrinsic viscosity, as determined in chloroform at 25°C, of about 0.3 to about 1.5 deciliters per gram (dl/gm), specifically about 0.45 to about 1.0 dl/gm. The copolyester-poly carbonate resins may have a weight average molecular weight of about 10,000 to about 200,000, specifically about 20,000 to about 100,000 as measured by gel permeation chromatography. The copolyester-poly carbonate resins are substantially free of impurities, residual acids, residual bases, and/or residual metals that may catalyze the hydrolysis of polycarbonate.

The polycarbonate component may further comprise, in addition to the polycarbonates described above, combinations of the polycarbonates with other thermoplastic polymers, for example combinations of polycarbonate homopolymers and/or copolymers with polyesters and the like. As used herein, a “combination” is inclusive of all mixtures, blends, alloys, and the like. Suitable polyesters comprise repeating units of formula (6), and may be, for example, poly(alkylene dicarboxylates), liquid crystalline polyesters, and polyester copolymers. It is also possible to use a branched polyester in which a branching agent, for example, a glycol having three or more hydroxyl groups or a trifunctional or multifunctional carboxylic acid has been incorporated. Furthermore, it is sometime desirable to have various concentrations of acid and hydroxyl end groups on the polyester, depending on the ultimate end-use of the composition.

In one embodiment, poly(alkylene terephthalates) are used. Specific examples of suitable poly(alkylene terephthalates) are poly(ethylene terephthalate) (PET), poly(1,4-butylene terephthalate) (PBT), poly(ethylene naphthanoate) (PEN), poly(butylene terephthalate), (PBN), (polypropylene terephthalate) (PPT), polycyclohexanedimethanol terephthalate (PCT), and combinations comprising at least one of the foregoing polyesters. Also contemplated herein are the above polyesters with a minor amount, e.g., from about 0.5 to about 10 percent by weight, of units derived from an aliphatic diacid and/or an aliphatic polyol to make copolyesters.
The blends of a polycarbonate and a polyester may comprise about 10 to about 99 wt.% polycarbonate and correspondingly about 1 to about 90 wt.% polyester, in particular a poly(alkylene terephthalate). In one embodiment, the blend comprises about 30 to about 70 wt.% polycarbonate and correspondingly about 30 to about 70 wt.% polyester. The foregoing amounts are based on the combined weight of the polycarbonate and polyester.

Although blends of polycarbonates with other polymers are contemplated, in one embodiment the polycarbonate component consists essentially of polycarbonate, i.e., the polycarbonate component comprises polycarbonate homopolymers and/or polycarbonate copolymers, and no other resins that would significantly adversely impact the hydrolytic stability, thermal stability, and/or impact strength of the thermoplastic composition. In another embodiment, the polycarbonate component consists of polycarbonate, i.e., is composed of only polycarbonate homopolymers and/or polycarbonate copolymers.

The thermoplastic composition further includes an impact modifier composition and other optional additives that are essentially free of species that can cause the degradation of polycarbonate. As used herein “degradation of polycarbonates” means a measurable decrease in the molecular weight of the polycarbonates, and includes but is not limited to transesterification and/or hydrolytic degradation. Such degradation may occur over time, and may be accelerated by conditions of humidity and/or heat. Methods for the measurement of polycarbonate degradation are known, and include, for example, determination of change in spiral flow, melt viscosity, melt volume, molecular weight and the like.

Species that can cause the degradation of polycarbonate include but are not limited to impurities, by-products, and residual compounds used in the manufacture of the components of the impact modifier composition, for example certain residual acids, residual bases, residual emulsifiers, and/or residual metals, for example alkali metals, that may catalyze the degradation of polycarbonate. As used herein, a “species” is inclusive of any form of material that can cause the degradation of a polycarbonate, for example, a compound, an anion, a cation, a salt, a bulk material, and the like.
Further as used herein, a species may "cause" the degradation of a polycarbonate directly, for example, by participating in the degradation as a catalyst, for example, or indirectly. For example, a species may indirectly cause the degradation of polycarbonate by reacting with another material in the composition to generate a third species that then causes the degradation of the polycarbonate.

One method of determining whether a component such as an impact modifier or other additive is essentially free of species that can cause the degradation of polycarbonate is to measure the pH of a slurry or solution of the individual component(s). In one embodiment, a slurry of the component has a pH of about 4 to about 8, specifically about 5 to about 7, and more specifically about 6 to about 7. While the pH of a combination of the components may be determined, determining the pH of each component individually may more accurately reflect the presence of species that degrade polycarbonates. Alternatively, the component can be extracted with water and the pH of the aqueous layer determined. In some cases it may be effective to adjust the pH of a slurry or solution of a component prior to admixture with the remaining components in order to prevent degradation of a polycarbonate.

Another method of determining whether a component is essentially free of a species that can cause the degradation of a polycarbonate is to analyze the component for specific species. In one embodiment, each component of the thermoplastic composition has an alkali metal content that is undetectable at an analytical sensitivity of 1 part per million (ppm). Alternatively, each component has an alkali metal content of less than about 1 ppm, specifically less than about 0.1 ppm, and more specifically less than about 0.01 ppm. In still another embodiment, the sodium and potassium content of each of the components is less than about 1 ppm, more specifically less than about 0.1 ppm. In still another embodiment, the sodium carbonate and potassium carbonate content of each of the components is less than about 1 ppm, more specifically less than about 0.1 ppm.

In another embodiment, each component of the thermoplastic composition has an amine content of less than about 50 ppm, specifically less than about 1 ppm. In still another embodiment, each component of the thermoplastic composition has an
ammonia content of less than about 100 ppm, specifically less than about 1 ppm. The amide content of each component may be less than about 100 ppm, specifically less than about 1 ppm. Good hydrolytic and/or thermal stability results may be obtained where each component of the thermoplastic composition meets a combination comprising at least one of the foregoing limitations with respect to alkali metals, amines, ammonia, and amides, and particularly where each component of the thermoplastic composition has an alkali metal content that is non-detectable at an analytical detectability limit of 1 ppm, an amine content of less than 50 ppm, an ammonia content of less than 100 ppm, and an amide content of less than about 100 ppm.

It has been found by the inventors hereof that an effective impact modifier composition accordingly comprises a bulk polymerized ABS together with one or more additional impact modifiers that are essentially free of species that degrade polycarbonates. Use of such impact modifiers can provide thermoplastic compositions having excellent hydrolytic stability and/or thermal stability.

The bulk polymerized ABS comprises an elastomeric phase comprising (i) butadiene and having a Ts of less than about 10°C, and (ii) a rigid polymeric phase having a Tg of greater than about 15°C and comprising a copolymer of a monovinylaromatic monomer such as styrene and an unsaturated nitrile such as acrylonitrile. Such ABS polymers may be prepared by first providing the elastomeric polymer, then polymerizing the constituent monomers of the rigid phase in the presence of the elastomer to obtain the graft copolymer. The grafts may be attached as graft branches or as shells to an elastomer core. The shell may merely physically encapsulate the core, or the shell may be partially or essentially completely grafted to the core.

Polybutadiene homopolymer may be used as the elastomer phase. Alternatively, the elastomer phase of the bulk polymerized ABS comprises butadiene copolymerized with up to about 25 wt.% of another conjugated diene monomer of formula (8):

![](image)

(8)
wherein each $X^b$ is independently C$_1$-C$_5$ alkyl. Examples of conjugated diene monomers that may be used are isoprene, 1,3-heptadiene, methyl-1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, 2-ethyl-1,3-pentadiene; 1,3- and 2,4-hexadienes, and the like, as well as mixtures comprising at least one of the foregoing conjugated diene monomers. A specific conjugated diene is isoprene.

The elastomeric butadiene phase may additionally be copolymerized with up to 25 wt%, specifically up to about 15 wt.%, of another comonomer, for example monovinylaromatic monomers containing condensed aromatic ring structures such as vinyl naphthalene, vinyl anthracene and the like, or monomers of formula (9):

![Diagram](image)

(9)

wherein each $X^c$ is independently hydrogen, C$_1$-C$_{12}$ alkyl, C$_3$-C$_{12}$ cycloalkyl, C$_6$-C$_{12}$ aryl, C$_7$-C$_{12}$ aralkyl, C$_7$-C$_{12}$ alkaryl, C$_1$-C$_{12}$ alkoxy, C$_3$-C$_{12}$ cycloalkoxy, C$_6$-C$_{12}$ aryloxy, chloro, bromo, or hydroxy, and R is hydrogen, C$_1$-C$_5$ alkyl, bromo, or chloro. Examples of suitable monovinylaromatic monomers copolymerizable with the butadiene include styrene, 3-methylstyrene, 3,5-dimethylstyrene, 4-n-propylstyrene, alpha-methylstyrene, alpha-methyl vinyltoluene, alpha-chlorostyrene, alpha-bromostyrene, dichlorostyrene, dibromostyrene, tetra-chlorostyrene, and the like, and combinations comprising at least one of the foregoing monovinylaromatic monomers. In one embodiment, the butadiene is copolymerized with up to about 12 wt.%, specifically about 1 to about 10 wt.% styrene and/or alpha-methyl styrene.

Other monomers that may be copolymerized with the butadiene are monovinylc monomers such as itaconic acid, acrylamide, N-substituted acrylamide or methacrylamide, maleic anhydride, maleimide, N-alkyl-, aryl-, or haloaryl-substituted maleimide, glycidyl (meth)acrylates, and monomers of the generic formula (10):

![Diagram](image)

(10)
wherein R is hydrogen, C₁⁻C₅ alkyl, bromo, or chloro, and X⁺ is cyano, C₁⁻C₁₂ alkoxy carbonyl, C₁⁻C₁₂ aryloxy carbonyl, hydroxy carbonyl, and the like. Examples of monomers of formula (10) include acrylonitrile, ethacrylonitrile, methacrylonitrile, alpha-chloroacrylonitrile, beta-chloroacrylonitrile, alpha-bromoacrylonitrile, acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, t-butyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, and the like, and combinations comprising at least one of the foregoing monomers. Monomers such as n-butyl acrylate, ethyl acrylate, and 2-ethylhexyl acrylate, are commonly used as monomers copolymerizable with the butadiene.

The particle size of the butadiene phase is not critical, and may be, for example about 0.01 to about 20 micrometers, specifically about 0.5 to about 10 micrometers, more specifically about 0.6 to about 1.5 micrometers may be used for bulk polymerized rubber substrates. Particle size may be measured by light transmission methods or capillary hydrodynamic chromatography (CHDF). The butadiene phase may provide about 5 to about 95 wt.% of the total weight of the ABS impact modifier copolymer, more specifically about 20 to about 90 wt.%, and even more specifically about 40 to about 85 wt.% of the ABS impact modifier, the remainder being the rigid graft phase.

The rigid graft phase comprises a copolymer formed from a styrenic monomer composition together with an unsaturated monomer comprising a nitrile group. As used herein, “styrenic monomer” includes monomers of formula (9) wherein each X⁺ is independently hydrogen, C₁⁻C₄ alkyl, phenyl, C₇⁻C₉ aralkyl, C₁⁻C₄ alkoxy, phenoxy, chloro, bromo, or hydroxy, and R is hydrogen, C₁⁻C₂ alkyl, bromo, or chloro. Specific examples styrene, 3-methylstyrene, 3,5-diethylstyrene, 4-n-propylstyrene, alpha-methylstyrene, alpha-methyl vinyltoluene, alpha-chlorostyrene, alpha-bromostyrene, dichlorostyrene, dibromostyrene, tetra-chlorostyrene, and the like. Combinations comprising at least one of the foregoing styrenic monomers may be used.

Further as used herein, an unsaturated monomer comprising a nitrile group includes monomers of formula (10) wherein R is hydrogen, C₁⁻C₅ alkyl, bromo, or chloro, and
X is cyano. Specific examples include acrylonitrile, ethacrylonitrile, methacrylonitrile, alpha-chloroacrylonitrile, beta-chloroacrylonitrile, alpha-bromoacrylonitrile, and the like. Combinations comprising at least one of the foregoing monomers may be used.

The rigid graft phase of the bulk polymerized ABS may further optionally comprise other monomers copolymerizable therewith, including other monovinylaromatic monomers and/or monovinyl monomers such as itaconic acid, acrylamide, N-substituted acrylamide or methacrylamide, maleic anhydride, maleimide, N-alkyl-, aryl-, or haloaryl-substituted maleimide, glycidyl (meth)acrylates, and monomers of the generic formula (10). Specific comonomers include C1-C4 alkyl (meth)acrylates, for example methyl methacrylate.

The rigid copolymer phase will generally comprise about 10 to about 99 wt.%, specifically about 40 to about 95 wt.%, more specifically about 50 to about 90 wt.% of the styrenic monomer; about 1 to about 90 wt.%, specifically about 10 to about 80 wt. %, more specifically about 10 to about 50 wt.% of the unsaturated monomer comprising a nitrile group; and 0 to about 25 wt.%, specifically 1 to about 15 wt.% of other comonomer, each based on the total weight of the rigid copolymer phase.

The bulk polymerized ABS copolymer may further comprise a separate matrix or continuous phase of ungrafted rigid copolymer that may be simultaneously obtained with the ABS. The ABS may comprise about 40 to about 95 wt.% elastomer-modified graft copolymer and about 5 to about 65 wt.% rigid copolymer, based on the total weight of the ABS. In another embodiment, the ABS may comprise about 50 to about 85 wt.%, more specifically about 75 to about 85 wt.% elastomer-modified graft copolymer, together with about 15 to about 50 wt.%, more specifically about 15 to about 25 wt.% rigid copolymer, based on the total weight of the ABS.

A variety of bulk polymerization methods for ABS-type resins are known. In multizone plug flow bulk processes, a series of polymerization vessels (or towers), consecutively connected to each other, providing multiple reaction zones. The elastomeric butadiene may be dissolved in one or more of the monomers used to form
the rigid phase, and the elastomer solution is fed into the reaction system. During the reaction, which may be thermally or chemically initiated, the elastomer is grafted with the rigid copolymer (i.e., SAN). Bulk copolymer (referred to also as free copolymer, matrix copolymer, or non-grafted copolymer) is also formed within the continuous phase containing the dissolved rubber. As polymerization continues, domains of free copolymer are formed within the continuous phase of rubber/comonomers to provide a two-phase system. As polymerization proceeds, and more free copolymer is formed, the elastomer-modified copolymer starts to disperse itself as particles in the free copolymer and the free copolymer becomes a continuous phase (phase inversion). Some free copolymer is generally occluded within the elastomer-modified copolymer phase as well. Following the phase inversion, additional heating may be used to complete polymerization. Numerous modifications of this basis process have been described, for example in U.S. Patent No. 3,511,895, which describes a continuous bulk ABS process that provides controllable molecular weight distribution and microgel particle size using a three-stage reactor system. In the first reactor, the elastomer/monomer solution is charged into the reaction mixture under high agitation to precipitate discrete rubber particle uniformly throughout the reactor mass before appreciable cross-linking can occur. Solids levels of the first, the second, and the third reactor are carefully controlled so that molecular weights fall into a desirable range. U.S. Patent No. 3,981,944 discloses extraction of the elastomer particles using the styrenic monomer to dissolve/disperse the elastomer particles, prior to addition of the unsaturated monomer comprising a nitrile group and any other comonomers. U.S. Patent No. 5,414,045 discloses reacting in a plug flow grafting reactor a liquid feed composition comprising a styrenic monomer composition, an unsaturated nitrile monomer composition, and an elastomeric butadiene polymer to a point prior to phase inversion, and reacting the first polymerization product (grafted elastomer) therefrom in a continuous-stirred tank reactor to yield a phase inverted second polymerization product that then can be further reacted in a finishing reactor, and then devolatilized to produce the desired final product.

In addition to the bulk polymerized ABS, the impact modifier composition comprises an additional impact modifier that is different than the ABS. These impact modifiers
include elastomer-modified graft copolymers comprising (i) an elastomeric (i.e., rubbery) polymer substrate having a Tg less than about 10°C, more specifically less than about -10°C, or more specifically about -40°C to -80°C, and (ii) a rigid polymeric superstrate grafted to the elastomeric polymer substrate. The grafts may be attached as graft branches or as shells to an elastomer core. The shell may merely physically encapsulate the core, or the shell may be partially or essentially completely grafted to the core.

Suitable materials for use as the elastomer phase include, for example, conjugated diene rubbers; copolymers of a conjugated diene with less than about 50 wt.% of a copolymerizable monomer; olefin rubbers such as ethylene propylene copolymers (EPR) or ethylene-propylene-diene monomer rubbers (EPDM); ethylene-vinyl acetate rubbers; silicone rubbers; elastomeric C_{1-8} alkyl (meth)acrylates; elastomeric copolymers of C_{1-8} alkyl (meth)acrylates with butadiene and/or styrene; or combinations comprising at least one of the foregoing elastomers.

Suitable conjugated diene monomers for preparing the elastomer phase are of formula (8) above wherein each \( X^b \) is independently hydrogen, C_{1-5} alkyl, and the like. Examples of conjugated diene monomers that may be used are butadiene, isoprene, 1,3-heptadiene, methyl-1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, 2-ethyl-1,3-pentadiene; 1,3- and 2,4-hexadienes, and the like, as well as mixtures comprising at least one of the foregoing conjugated diene monomers. Specific conjugated diene homopolymers include polybutadiene and polyisoprene.

Copolymers of a conjugated diene rubber may also be used, for example those produced by aqueous radical emulsion polymerization of a conjugated diene and one or more monomers copolymerizable therewith. Monomers that are suitable for copolymerization with the conjugated diene include monovinylaromatic monomers containing condensed aromatic ring structures, such as vinyl naphthalene, vinyl anthracene and the like, or monomers of formula (9) above, wherein each \( X^c \) is independently hydrogen, C_{1-12} alkyl, C_{3-12} cycloalkyl, C_{6-12} aryl, C_{7-12} aralkyl, C_{7-12} alkaryl, C_{1-12} alkoxy, C_{3-12} cycloalkoxy, C_{6-12} aryloxy, chloro, bromo, or hydroxy, and \( R \) is hydrogen, C_{1-5} alkyl, bromo, or chloro. Examples of suitable
monovinylaromatic monomers that may be used include styrene, 3-methylstyrene, 3,5-diethylstyrene, 4-n-propylstyrene, alpha-methylstyrene, alpha-methylvinyltoluene, alpha-chlorostyrene, alpha-bromostyrene, dichlorostyrene, dibromostyrene, tetra-chlorostyrene, combinations comprising at least one of the foregoing compounds, and the like. Styrene and/or alpha-methylstyrene are commonly used as monomers copolymerizable with the conjugated diene monomer.

Other monomers that may be copolymerized with the conjugated diene are monovinyl monomers such as itaconic acid, acrylamide, N-substituted acrylamide or methacrylamide, maleic anhydride, maleimide, N-alkyl-, aryl-, or haloaryl-substituted maleimide, glycidyl (meth)acrylates, and monomers of the generic formula (10) wherein R is hydrogen, C₁₋₅ alkyl, bromo, or chloro, and R₅ is cyano, C₁₋₁₂ alkoxyacrylonitrile, C₁₋₁₂ aryloxycarbonyl, hydroxy carbonyl, and the like. Examples of monomers of formula (10) include acrylonitrile, ethacrylonitrile, methacrylonitrile, alpha-chloroacrylonitrile, beta-chloroacrylonitrile, alpha-bromoacrylonitrile, acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, t-butyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, and the like, and combinations comprising at least one of the foregoing monomers. Monomers such as n-butyl acrylate, ethyl acrylate, and 2-ethylhexyl acrylate are commonly used as monomers copolymerizable with the conjugated diene monomer. Mixtures of the foregoing monovinyl monomers and monovinylaromatic monomers may also be used.

Certain (meth)acrylate monomers may also be used to provide the elastomer phase, including cross-linked, particulate emulsion homopolymers or copolymers of C₁₋₁₆ alkyl (meth)acrylates, specifically C₁₋₉ alkyl (meth)acrylates, in particular C₄₋₆ alkyl acrylates, for example n-butyl acrylate, t-butyl acrylate, n-propyl acrylate, isopropyl acrylate, 2-ethylhexyl acrylate, and the like, and combinations comprising at least one of the foregoing monomers. The C₁₋₁₆ alkyl (meth)acrylate monomers may optionally be polymerized in admixture with up to 15 wt.% of comonomers of generic formulas (8), (9), or (10) as broadly described above. Exemplary comonomers include but are not limited to butadiene, isoprene, styrene, methyl methacrylate, phenyl methacrylate, phenethylmethacrylate, N-cyclohexylacrylamide, vinyl methyl ether or acrylonitrile,
and mixtures comprising at least one of the foregoing comonomers. Optionally, up to 5 wt.% a polyfunctional crosslinking comonomer may be present, for example divinylbenzene, alkyleneol di(meth)acrylates such as glycol bisacrylate, alkylenetrioil tri(meth)acrylates, polyester di(meth)acrylates, bisacrylamides, triallyl cyanurate, triallyl isocyanurate, allyl (meth)acrylate, diallyl maleate, diallyl fumarate, diallyl adipate, triallyl esters of citric acid, triallyl esters of phosphoric acid, and the like, as well as combinations comprising at least one of the foregoing crosslinking agents.

The elastomer phase may be polymerized by mass, emulsion, suspension, solution or combined processes such as bulk-suspension, emulsion-bulk, bulk-solution or other techniques, using continuous, semibatch, or batch processes. The particle size of the elastomer substrate is not critical. For example, an average particle size of about 0.001 to about 25 micrometers, specifically about 0.01 to about 15 micrometers, or even more specifically about 0.1 to about 8 micrometers may be used for emulsion based polymerized rubber lattices. A particle size of about 0.5 to about 10 micrometers, specifically about 0.6 to about 1.5 micrometers may be used for bulk polymerized rubber substrates. The elastomer phase may be a particulate, moderately cross-linked copolymer derived from conjugated butadiene or C₄₋₆ alkyl acrylate rubber, and preferably has a gel content greater than 70%. Also suitable are copolymers derived from mixtures of butadiene with styrene, acrylonitrile, and/or C₄₋₆ alkyl acrylate rubbers.

The elastomeric phase may provide about 5 to about 95 wt.% of the elastomer-modified graft copolymer, more specifically about 20 to about 90 wt.%, and even more specifically about 40 to about 85 wt.%, the remainder being the rigid graft phase.

The rigid phase of the elastomer-modified graft copolymer may be formed by graft polymerization of a mixture comprising a monovinylaromatic monomer and optionally one or more comonomers in the presence of one or more elastomeric polymer substrates. The above broadly described monovinylaromatic monomers of formula (9) may be used in the rigid graft phase, including styrene, alpha-methyl
styrene, halostyrenes such as dibromostyrene, vinyltoluene, vinylxylene, butylstyrene, para-hydroxystyrene, methoxystyrene, and the like, or combinations comprising at least one of the foregoing monovinylaromatic monomers. Suitable comonomers include, for example, the above broadly described monovinylic monomers and/or monomers of the general formula (10). In one embodiment, R is hydrogen or C₁-C₂ alkyl, and X⁺ is cyano or C₁-C₁₂ alkoxy carbonyl. Specific examples of suitable comonomers for use in the rigid phase include acrylonitrile, ethacrylonitrile, methacrylonitrile, methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, and the like, and combinations comprising at least one of the foregoing comonomers.

In one specific embodiment, the rigid graft phase is formed from styrene or alpha-methyl styrene copolymerized with ethyl acrylate and/or methyl methacrylate. In other specific embodiments, the rigid graft phase is formed from styrene copolymerized with; styrene copolymerized with methyl methacrylate; and styrene copolymerized with methyl methacrylate and acrylonitrile.

The relative ratio of monovinylaromatic monomer and comonomer in the rigid graft phase may vary widely depending on the type of elastomer substrate, type of monovinylaromatic monomer(s), type of comonomer(s), and the desired properties of the impact modifier. The rigid phase may generally comprise up to 100 wt.% of monovinyl aromatic monomer, specifically about 30 to about 100 wt.%, more specifically about 50 to about 90 wt.% monovinylaromatic monomer, with the balance being comonomer(s).

Depending on the amount of elastomer-modified polymer present, a separate matrix or continuous phase of ungrafted rigid polymer or copolymer may be simultaneously obtained along with the additional elastomer-modified graft copolymer. Typically, such impact modifiers comprise about 40 to about 95 wt.% elastomer-modified graft copolymer and about 5 to about 65 wt.% rigid (co)polymer, based on the total weight of the impact modifier. In another embodiment, such impact modifiers comprise about 50 to about 85 wt.%, more specifically about 75 to about 85 wt.% rubber-modified rigid copolymer, together with about 15 to about 50 wt.%, more specifically
about 15 to about 25 wt.% rigid (co)polymer, based on the total weight of the impact modifier.

Specific examples of elastomer-modified graft copolymers that differ from the bulk polymerized ABS include but are not limited to acrylonitrile-styrene-butyl acrylate (ASA), methyl methacrylate-acrylonitrile-butadiene-styrene (MABS), methyl methacrylate-butadiene-styrene (MBS), and acrylonitrile-ethylene-propylene-diene-styrene (AES). The MBS resins may be prepared by emulsion polymerization of methacrylate and styrene in the presence of polybutadiene as is described in U.S. Patent No. 6,545,089, which process is summarized below.

Another specific type of elastomer-modified impact modifier that differs from the bulk polymerized ABS copolymer comprises structural units derived from at least one silicone rubber monomer, a branched acrylate rubber monomer having the formula H₂C=CRᵗC(O)OCH₂CH₂Rᵗ, wherein Rᵗ is hydrogen or a C₁₋C₉ linear or branched hydrocarbyl group and Rᵗ is a branched C₃₋C₁₅ hydrocarbyl group; a first graft link monomer; a polymerizable alkenyl-containing organic material; and a second graft link monomer. The silicone rubber monomer may comprise, for example, a cyclic siloxane, tetraalkoxysilane, trialkoxysilane, (acyrloxy)alkoxysilane, (mercaptoalkyl)alkoxysilane, vinylalkoxysilane, or allylalkoxysilane, alone or in combination, e.g., decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, trimethyltriphenylcyclotrisiloxane, tetramethyltetraphenylcyclotetrasiloxane, tetramethyltetravinylcyclotetrasiloxane, octaphenylcyclotetrasiloxane, octamethylcyclotetrasiloxane and/or tetraethoxysilane.

Exemplary branched acrylate rubber monomers include iso-octyl acrylate, 6-methyloctyl acrylate, 7-methyloctyl acrylate, 6-methylheptyl acrylate, and the like, alone or in combination. The polymerizable alkenyl-containing organic material may be, for example, a monomer of formula (9) or (10), e.g., styrene, alpha-methylstyrene, acrylonitrile, methacrylonitrile, or an unbranched (meth)acrylate such as methyl methacrylate, 2-ethylhexyl methacrylate, methyl acrylate, ethyl acrylate, n-propyl acrylate, and the like, alone or in combination.
The at least one first graft link monomer may be an (acyloxy)alkoxysilane, a (mercaptoalkyl)alkoxysilane, a vinylalkoxysilane, or an allylalkoxysilane, alone or in combination, e.g., (gamma-methacryloxypropyl)(dimethoxy)methylsilane and/or (3-mercaptopropyl)trimethoxysilane. The at least one second graft link monomer is a polyethylenically unsaturated compound having at least one allyl group, such as allyl methacrylate, triallyl cyanurate, or triallyl isocyanurate, alone or in combination.

The silicone-acrylate impact modifier compositions can be prepared by emulsion polymerization, wherein, for example at least one silicone rubber monomer is reacted with at least one first graft link monomer at a temperature from about 30°C to about 110°C to form a silicone rubber latex, in the presence of a surfactant such as dodecylbenzenesulfonic acid. Alternatively, a cyclic siloxane such as cyclooctamethyltetrasiloxane and an tetraethoxyorthosilicate may be reacted with a first graft link monomer such as (gamma-methacryloxypropyl)methyltrimethoxysilane, to afford silicone rubber having an average particle size from about 100 nanometers to about 2 microns. At least one branched acrylate rubber monomer is then polymerized with the silicone rubber particles, optionally in presence of a cross linking monomer, such as allyl methacrylate in the presence of a free radical generating polymerization catalyst such as benzyol peroxide. This latex is then reacted with a polymerizable alkenyl-containing organic material and a second graft link monomer. The latex particles of the graft silicone-acrylate rubber hybrid may be separated from the aqueous phase through coagulation (by treatment with a coagulant) and dried to a fine powder to produce the silicone-acrylate rubber impact modifier composition. This method can be generally used for producing the silicone-acrylate impact modifier having a particle size from about 100 nanometers to about two micrometers.

In practice, any of the above described impact modifiers different from the bulk polymerized ABS may be used, providing it is essentially free of any species that cause the degradation of a polycarbonate. Processes for the formation of the elastomer-modified graft copolymers include mass, emulsion, suspension, and solution processes, or combined processes such as bulk-suspension, emulsion-bulk, bulk-solution or other techniques, using continuous, semibatch, or batch processes.
Such processes may be conducted so as to avoid the use or production of any species that degrade polycarbonates, and/or to provide the additional impact modifiers with the desired pH.

In one embodiment, the impact modifier is prepared by an emulsion polymerization process that avoids the use or production of any species that degrade polycarbonates. In another embodiment the impact modifier is prepared by an emulsion polymerization process that is free of basic species, for example species such as alkali metal salts of C_{6-30} fatty acids, for example sodium stearate, lithium stearate, sodium oleate, potassium oleate, and the like, alkali metal carbonates, amines such as dodecyl dimethyl amine, dodecyl amine, and the like, and ammonium salts of amines. Such materials are commonly used as polymerization aids, e.g., surfactants in emulsion polymerization, and may catalyze transesterification and/or degradation of polycarbonates. Instead, ionic sulfate, sulfonate or phosphate surfactants may be used in preparing the impact modifiers, particularly the elastomeric substrate portion of the impact modifiers. Suitable surfactants include, for example, C_{1-22} alkyl or C_{7-25} alkylaryl sulfonates, C_{1-22} alkyl or C_{7-25} alkylaryl sulfates, C_{1-22} alkyl or C_{7-25} alkylaryl phosphates, substituted silicates, and combinations comprising at least one of the foregoing surfactants. A specific surfactant is a C_{6-16}, specifically a C_{8-12} alkyl sulfonate. This emulsion polymerization process is described and disclosed in various patents and literature of such companies as Rohm & Haas and General Electric Company.

In addition to the bulk polymerized ABS and the additional impact modifier differing from the bulk polymerized ABS, the impact modifier composition may further comprise an ungrafted rigid copolymer. The rigid copolymer is additional to any rigid copolymer present in the bulk polymerized ABS or additional impact modifier. It may be the same as any of the rigid copolymers described above, without the elastomer modification. The rigid copolymers generally have a Tg greater than about 15°C, specifically greater than about 20°C, and include, for example, polymers derived from monovinylaromatic monomers containing condensed aromatic ring structures, such as vinyl naphthalene, vinyl anthracene and the like, or monomers of formula (9) as broadly described above, for example styrene and alpha-methyl
styrene; monovinylic monomers such as itaconic acid, acrylamide, N-substituted acrylamide or methacrylamide, maleic anhydride, maleimide, N-alkyl, aryl or haloaryl substituted maleimide, glycidyl (meth)acrylates, and monomers of the general formula (10) as broadly described above, for example acrylonitrile, methyl acrylate and methyl methacrylate; and copolymers of the foregoing, for example styrene-acrylonitrile (SAN), styrene-alpha-methyl styrene-acrylonitrile, methyl methacrylate-acrylonitrile-styrene, and methyl methacrylate-styrene.

The rigid copolymer may comprise about 1 to about 99 wt.%, specifically about 20 to about 95 wt.%, more specifically about 40 to about 90 wt.% of vinylaromatic monomer, together with 1 to about 99 wt.%, specifically about 5 to about 80 wt.%, more specifically about 10 to about 60 wt.% of copolymerizable monovinylic monomers. In one embodiment the rigid copolymer is SAN, which may comprise about 50 to about 99 wt.% styrene, with the balance acrylonitrile, specifically about 60 to about 90 wt.% styrene, and more specifically about 65 to about 85 wt.% styrene, with the remainder acrylonitrile.

The rigid copolymer may be manufactured by bulk, suspension, or emulsion polymerization, and is substantially free of impurities, residual acids, residual bases or residual metals that may catalyze the hydrolysis of polycarbonate. In one embodiment, the rigid copolymer is manufactured by bulk polymerization using a boiling reactor. The rigid copolymer may have a weight average molecular weight of about 50,000 to about 300,000 as measured by GPC using polystyrene standards. In one embodiment, the weight average molecular weight of the rigid copolymer is about 70,000 to about 190,000.

The relative amount of each component of the thermoplastic composition will depend on the particular type of polycarbonate(s) used, the presence of any other resins, and the particular impact modifiers, including any rigid graft copolymer, as well as the desired properties of the composition. Particular amounts may be readily selected by one of ordinary skill in the art using the guidance provided herein.
In one embodiment, the thermoplastic composition comprises about 1 to about 95 wt.% polycarbonate component, about 5 to about 98 wt.% bulk polymerized ABS, and about 1 to about 95 wt.% additional elastomer-modified impact modifier. In another embodiment, the thermoplastic composition comprises about 10 to about 90 wt.% polycarbonate component, about 5 to about 75 wt.% bulk polymerized ABS, and about 1 to about 30 wt.% other elastomer-modified impact modifier. In another embodiment, the thermoplastic composition comprises about 20 to about 84 wt.% polycarbonate component, about 5 to about 50 wt.% bulk polymerized ABS, and about 4 to about 20 wt.% additional elastomer-modified impact modifier. In another embodiment, the thermoplastic composition comprises about 64 to about 74 wt.% polycarbonate component, about 5 to about 35 wt.% bulk polymerized ABS, and about 2 to about 10 wt.% additional elastomer-modified impact modifier. In another embodiment, the thermoplastic composition comprises about 68 to about 72 wt.% polycarbonate component, about 17 to about 23 wt.% bulk polymerized ABS, and about 4 to about 8 wt.% additional elastomer-modified impact modifier. The foregoing compositions may further comprise 0 about 50 wt.%, specifically 0 to about 35 wt.%, more specifically about 1 to about 20 wt.%, even more specifically about 3 to about 8 wt.%, most specifically about 6 wt.% of a rigid copolymer. All of the foregoing amounts are based on the combined weight of the polycarbonate composition and the impact modifier composition.

As a specific example of the foregoing embodiments, there is provided a thermoplastic composition that comprises about 65 to about 75 wt.% of a polycarbonate component; about 16 to about 30 wt.% of a bulk polymerized ABS impact modifier; about 1 to about 10 wt.% of MBS; and 0 to about 6 wt.% of a rigid copolymer, for example SAN. Use of the foregoing amounts may provide compositions having enhanced hydrolytic stability together with good thermal stability and impact resistance, particularly at low temperatures.

In addition to the polycarbonate component and the impact modifier composition, the thermoplastic composition may include various additives such as fillers, reinforcing agents, stabilizers, and the like, with the proviso that the additives do not adversely affect the desired properties of the thermoplastic compositions, in particular
hydrolytic and/or thermal stability. Thus, additives that contain impurities or that would generate degradation catalysts in the presence of moisture and/or heat, for example hydrolytically unstable phosphites, may not be as desirable. Additives that may themselves as act as catalysts for the degradation of polycarbonates in the presence of moisture and/or heat may also not be desirable.

In one embodiment, each additive is essentially free of species that would cause the degradation of polycarbonates. As above, one method of determining whether an additive is essentially free of species that can cause the degradation of polycarbonate is to measure the pH of a slurry or solution of the individual additive(s). In one embodiment, a slurry of the additive has a pH of about 4 to about 8, specifically about 5 to about 7, and more specifically about 6 to about 7. While the pH of a combination of the additives may be determined, determining the pH of each component individually may more accurately reflect the presence of species that degrade polycarbonates. In some cases it may be effective to adjust the pH of a slurry or solution of a component prior to admixture with the remaining components.

In another embodiment, the additive may be treated to prevent or substantially reduce any degradative activity. Such treatments may include coating with a substantially inert substance such as silicone, acrylic, or epoxy resins. Treatment may also comprise chemical passivation to remove, block, or neutralize catalytic sites. A combination of treatments may be used. Additives such as fillers, reinforcing agents, and pigments may be treated.

Mixtures of additives may be used. Such additives may be mixed at a suitable time during the mixing of the components for forming the composition. Suitable fillers or reinforcing agents that may be used include, for example, silicates and silica powders such as aluminum silicate (mullite), synthetic calcium silicate, zirconium silicate, fused silica, crystalline silica graphite, natural silica sand, and the like; boron powders such as boron-nitride powder, boron-silicate powders, and the like; oxides such as TiO₂, aluminum oxide, magnesium oxide, and the like; calcium sulfate (as its anhydride, dihydrate or trihydrate); calcium carbonates such as chalk, limestone, marble, synthetic precipitated calcium carbonates, and the like; talc, including fibrous,
modular, needle shaped, lamellar talc, and the like; wollastonite; surface-treated wollastonite; glass spheres such as hollow and solid glass spheres, silicate spheres, cenospheres, aluminosilicate (armospheres), and the like; kaolin, including hard kaolin, soft kaolin, calcined kaolin, kaolin comprising various coatings known in the art to facilitate compatibility with the polymeric matrix resin, and the like; single crystal fibers or "whiskers" such as silicon carbide, alumina, boron carbide, iron, nickel, copper, and the like; fibers (including continuous and chopped fibers) such as asbestos, carbon fibers, glass fibers, such as E, A, C, ECR, R, S, D, or NE glasses, and the like; sulfides such as molybdenum sulfide, zinc sulfide and the like; barium species such as barium titanate, barium ferrite, barium sulfate, heavy spar, and the like; metals and metal oxides such as particulate or fibrous aluminum, bronze, zinc, copper and nickel and the like; flaked fillers such as glass flakes, flaked silicon carbide, aluminum diboride, aluminum flakes, steel flakes and the like; fibrous fillers, for example short inorganic fibers such as those derived from blends comprising at least one of aluminum silicates, aluminum oxides, magnesium oxides, and calcium sulfate hemihydrate and the like; natural fillers and reinforcements, such as wood flour obtained by pulverizing wood, fibrous products such as cellulose, cotton, sisal, jute, starch, cork flour, lignin, ground nut shells, corn, rice grain husks and the like; organic fillers such as polytetrafluoroethylene (Teflon) and the like; reinforcing organic fibrous fillers formed from organic polymers capable of forming fibers such as poly(ether ketone), polyimide, polybenzoxazole, poly(phenylene sulfide), polyesters, polyethylene, aromatic polyamides, aromatic polyimides, polyetherimides, polytetrafluoroethylene, acrylic resins, poly(vinyl alcohol) and the like; as well as additional fillers and reinforcing agents such as mica, clay, feldspar, flue dust, fillite, quartz, quartzite, perlite, tripoli, diatomaceous earth, carbon black, and the like, and combinations comprising at least one of the foregoing fillers and reinforcing agents. The fillers/reinforcing agents may be coated to prevent reactions with the matrix or may be chemically passivated to neutralize catalytic degradation site that might promote hydrolytic or thermal degradation.

The fillers and reinforcing agents may be coated with a layer of metallic material to facilitate conductivity, or surface treated with silanes to improve adhesion and
dispersion with the polymeric matrix resin. In addition, the reinforcing fillers may be provided in the form of monofilament or multifilament fibers and may be used either alone or in combination with other types of fiber, through, for example, co-weaving or core/sheath, side-by-side, orange-type or matrix and fibril constructions, or by other methods known to one skilled in the art of fiber manufacture. Suitable co-woven structures include, for example, glass fiber-carbon fiber, carbon fiber-aromatic polyimide (aramid) fiber, and aromatic polyimide fiberglass fiber and the like. Fibrous fillers may be supplied in the form of, for example, rovings, woven fibrous reinforcements, such as 0-90 degree fabrics and the like; non-woven fibrous reinforcements such as continuous strand mat, chopped strand mat, tissues, papers and felts and the like; or three-dimensional reinforcements such as braids. Fillers are generally used in amounts of about 0 to about 100 parts by weight, based on 100 parts by weight of the polycarbonate component and the impact modifier composition.

Suitable antioxidant additives include, for example, alkylated monophenols or polyphenols; alkylated reaction products of polyphenols with dienes, such as tetrakis[methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane, and the like; butylated reaction products of para-cresol or dicyclopentadiene; alkylated hydroquinones; hydroxylated thiodiphenyl ethers; alkylidene-bisphenols; benzyl species; esters of beta-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols; esters of beta-(5-tert-butyl-4-hydroxy-3-methylphenyl)-propionic acid with monohydric or polyhydric alcohols; and the like; and combinations comprising at least one of the foregoing antioxidants. Antioxidants are generally used in amounts of about 0.01 to about 1, specifically about 0.1 to about 0.5 parts by weight, based on 100 parts by weight of parts by weight of the polycarbonate component and the impact modifier composition.

Suitable heat and color stabilizer additives include, for example, organophosphites such as tris(2,4-di-tert-butyl phenyl) phosphite. Heat and color stabilizers are generally used in amounts of about 0.01 to about 5, specifically about 0.05 to about 0.3 parts by weight, based on 100 parts by weight of parts by weight of the polycarbonate component and the impact modifier composition.
Suitable secondary heat stabilizer additives include, for example thioethers and thioesters such as pentaerythritol tetrais (3-(dodecylthio)propionate), pentaerythritol tetrais[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], dilauryl thiodipropionate, distearyl thiodipropionate, dimyristyl thiodipropionate, ditridecyl thiodipropionate, pentaerythritol octylthiopropionate, dioctadecyl disulphide, and the like, and combinations comprising at least one of the foregoing heat stabilizers. Secondary stabilizers are generally used in amount of about 0.01 to about 5, specifically about 0.03 to about 0.3 parts by weight, based upon 100 parts by weight of parts by weight of the polycarbonate component and the impact modifier composition.

Light stabilizers, including ultraviolet light (UV) absorbing additives, may also be used. Suitable stabilizing additives of this type include, for example, benzotriazoles and hydroxybenzotriazoles such as 2-(2-hydroxy-5-methylphenyl)benzotriazole, 2-(2-hydroxy-5-tert-octylphenyl)-benzotriazole, 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol (CYASORB 5411 from Cytec), and TINUVIN 234 from Ciba Specialty Chemicals; hydroxybenzotriazines; hydroxyphenyl-triazine or -pyrimidine UV absorbers such as TINUVIN 1577 (Ciba), and 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]- 5-(octyloxy)-phenol (CYASORB 1164 from Cytec); non-basic hindered amine light stabilizers (hereinafter “HALS”), including substituted piperidine moieties and oligomers thereof, for example 4-piperidinol derivatives such as TINUVIN 622 (Ciba), GR-3034, TINUVIN 123, and TINUVIN 440; benzoazinones, such as 2,2'- (1,4-phenylene)bis(4H-3,1-benzoazin-4-one) (CYASORB UV-3638); hydroxybenzophenones such as 2-hydroxy-4-n-octyloxybenzophenone (CYASORB 531); oxanilides; cyanoacrylates such as 1,3-bis[(2-cyano-3,3-diphenylacryloyl)oxy]-2,2-bis[(2-cyano-3,3-diphenylacryloyl)oxy]methyl]propane (UVINUL 3030) and 1,3-bis[(2-cyano-3,3-diphenylacryloyl)oxy]-2,2-bis[(2-cyano-3,3-diphenylacryloyl)oxy]methyl]propane; and nano-size inorganic materials such as titanium oxide, cerium oxide, and zinc oxide, all with particle size less than about 100 nanometers; and the like, and combinations comprising at least one of the foregoing stabilizers. Light stabilizers may be used in amounts of about 0.01 to about 10, specifically about 0.1 to about 1 parts by weight, based on 100 parts by weight of parts by weight of the polycarbonate.
component and the impact modifier composition. UV absorbers are generally used in amounts of about 0.1 to about 5 parts by weight, based on 100 parts by weight of the polycarbonate component and the impact modifier composition.

Plasticizers, lubricants, and/or mold release agents additives may also be used. There is considerable overlap among these types of materials, which include, for example, phthalic acid esters such as dioctyl-4,5-epoxy-hexahydropthalate; tris-(octoxycarboxylethyl)isocyanurate; tristearin; di- or polyfunctional aromatic phosphates such as resorcinol tetraphenyl diphosphate (RDP), the bis(diphenyl) phosphate of hydroquinone and the bis(diphenyl) phosphate of bisphenol-A; poly-alpha-olefins; epoxidized soybean oil; silicones, including silicone oils; esters, for example, fatty acid esters such as alkyl stearyl esters, e.g., methyl stearate; stearyl stearate, pentadecytritol tetrastearate, and the like; mixtures of methyl stearate and hydrophilic and hydrophobic nonionic surfactants comprising polyethylene glycol polymers, polypropylene glycol polymers, and copolymers thereof, e.g., methyl stearate and polyethylene-polypropylene glycol copolymers in a suitable solvent; waxes such as beeswax, montan wax, paraffin wax and the like; and poly alpha olefins such as Ethylflo 164, 166, 168, and 170. Such materials are generally used in amounts of about 0.1 to about 20 parts by weight, specifically about 1 to about 10 parts by weight, based on 100 parts by weight of the polycarbonate component and the impact modifier composition.

Colorants such as pigment and/or dye additives may also be present. Suitable pigments include for example, inorganic pigments such as metal oxides and mixed metal oxides such as zinc oxide, titanium dioxides, iron oxides and the like; sulfides such as zinc sulfides, and the like; aluminates; sodium sulfo-silicates sulfates, chromates, and the like; carbon blacks; zinc ferrites; ultramarine blue; Pigment Brown 24; Pigment Red 101; Pigment Yellow 119; organic pigments such as azos, di-azos, quinacridones, perylenes, naphthalene tetracarboxylic acids, flavanthrones, isoindolinones, tetrachloroisoidolinones, anthraquinones, anthanthrones, dioxazines, phthalocyanines, and azo lakes; Pigment Blue 60, Pigment Red 122, Pigment Red 149, Pigment Red 177, Pigment Red 179, Pigment Red 202, Pigment Violet 29, Pigment Blue 15, Pigment Green 7, Pigment Yellow 147 and Pigment Yellow 150,
and combinations comprising at least one of the foregoing pigments. Pigments may be coated to prevent reactions with the matrix or may be chemically passivated to neutralize catalytic degradation site that might promote hydrolytic or thermal degradation. Pigments are generally used in amounts of about 0.01 to about 10 parts by weight, based on 100 parts by weight of parts by weight of the polycarbonate component and the impact modifier composition.

Suitable dyes are generally organic materials and include, for example, coumarin dyes such as coumarin 460 (blue), coumarin 6 (green), nile red and the like; lanthanide complexes; hydrocarbon and substituted hydrocarbon dyes; polycyclic aromatic hydrocarbon dyes; scintillation dyes such as oxazole or oxadiazole dyes; aryl- or heteroaryl-substituted poly (C_{2,8}) olefin dyes; carbocyanine dyes; indanthrone dyes; phthalocyanine dyes; oxazine dyes; carbostyril dyes; naphthalenetetracarboxylic acid dyes; porphyrin dyes; bis(styryl)biphenyl dyes; acridine dyes; anthraquinone dyes; cyanine dyes; methine dyes; arylmethane dyes; azo dyes; indigoid dyes, thioindigoid dyes, diazoniun dyes; nitro dyes; quinone imine dyes; aminoketone dyes; tetrazolium dyes; thiazole dyes; perylene dyes, perinone dyes; bis-benzoxazolylthiophene (BBOT); triarylmethane dyes; xanthene dyes; thioxanthene dyes; naphthalimide dyes; lactone dyes; fluorophores such as anti- stokes shift dyes which absorb in the near infrared wavelength and emit in the visible wavelength, and the like; luminescent dyes such as 5-amino-9-diethyliminobenz[a]phenoxazonium perchlorate; 7-amino-4-methylcarbostyril; 7-amino-4-methylcoumarin; 7-amino-4-trifluoromethylcoumarin; 3-(2'-benzimidazoyl)-7-N,N-diethylaminocoumarin; 3-(2'-benzothiazolyl)-7-diethylaminocoumarin; 2-(4-biphenylyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole; 2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole; 2-(4-biphenyl)-6-phenylbenzoxazole-1,3; 2,5-bis-(4-biphenylyl)-1,3,4-oxadiazole; 2,5-bis-(4-biphenylyl)-oxazoles; 4,4'-bis-(2-butyloctyloxy)-p-quaterphenyl; p-bis(o-methylstyrlyl)-benzene; 5,9-diaminobenzo(a)phenoxazonium perchlorate; 4-dicyanomethylene-2-methyl-6-(p-dimethyaminostyryl)-4H-pyran; 1,1'-diethyl-2,2'-carbocyanine iodide; 1,1'-diethyl-4,4'-carbocyanine iodide; 3,3'-diethyl-4,4',5,5'-dibenzothiatricarbocyanine iodide; 1,1'-diethyl-4,4'-dicarbocyanine iodide; 1,1'-diethyl-2,2'-dicarbocyanine iodide; 3,3'-diethyl-9,11-neopentylidenethiatricarbocyanine iodide; 1,3'-diethyl-4,2'
quinolyloxacarbocyanine iodide; 1,3'-diethyl-4,2'-quinolythiacarbocyanine iodide; 3-diethy lamino-7-diethyliminophenoxazonium perchlorate; 7-diethylamino-4-methylcoumarin; 7-diethylamino-4-trifluoromethylcoumarin; 7-diethylaminocoumarin; 3,3'-diethylxodiacarbocyanine iodide; 3,3'-diethylthiacarbocyanine iodide; 3,3'-diethylthiadiacarbocyanine iodide; 3,3'-diethylthiatricarbocyanine iodide; 4,6-dimethyl-7-ethylaminocoumarin; 2,2'-dimethyl-p-quaterphenyl; 2,2-dimethyl-p-terphenyl; 7-dimethylamino-1'-methyl-4-methoxy-8-azaquinolone-2; 7-dimethylamino-4-methylquinolone-2; 7-dimethylamino-4-trifluoromethylcoumarin; 2-(4-(4-dimethylaminophenyl)-1,3-butanediy1)-3-ethylbenzothiazolium perchlorate; 2-(6-(p-dimethylaminophenyl)-2,4-neopentylene-1,3,5-hexatrienyl)-3-methylbenzothiazolium perchlorate; 2-(4-(p-dimethylaminophenyl)-1,3-butanediyl)-1,3,3-trimethyl-3H-indolium perchlorate; 3,3'-dimethyloxatricarbocyanine iodide; 2,5-diphenylnifuran; 2,5-diphenyloxazole; 4,4'-diphenylstilbene; 1-ethyl-4-(4-(p-dimethylaminophenyl)-1,3-butanediy1)-pyridinium perchlorate; 1-ethyl-2-(4-(p-dimethylaminophenyl)-1,3-butanediy1)-pyridinium perchlorate; 1-ethyl-4-(4-(p-dimethylaminophenyl)-1,3-butanediyl)-quinolinium perchlorate; 3-ethylamino-7-ethylamino-2,8-dimethylphenoxazin-5-i um perchlorate; 9-ethylamino-5-ethylamino-10-methyl-5H-benzo(a) phenoxazonium perchlorate; 7-ethylamin o-6-methyl-4-trifluoromethylcoumarin; 7-ethylamino-4-trifluoromethylcoumarin; 1,1',3,3,3',3'-hexamethyl-4,4',5,5'-dibenzo-2,2'-indotricarbocyanine iodide; 1,1',3,3,3',3'-hexamethylandi dicarbocyanine iodide; 1,1',3,3,3',3'-hexamethylindotricarbocyanine iodide; 2-methyl-5-t-butyl-p-quaterphenyl; N-methyl-4-trifluoromethylpiperidino-<3,2-g>coumarin; 3-(2'-N-methylbenzimidazolyl)-7-N,N-diethylaminocoumarin; 2-(1-naphthyl)-5-phenyloxazole; 2,2'-p-phenylen-bis(5-phenyloxazole); 3,5,3'''',5''''-tetra-t-butyl-p-sexiphenyl; 3,5,3''',5''''-tetra-t-butyl-p-quinquephenyl; 2,3,5,6-1H,4H-tetrahydro-9-acetylquinolizino-<9,9a,1-gh>coumarin; 2,3,5,6-1H,4H-tetrahydro-9-carboethoxyquinolizino-<9,9a,1-gh>coumarin; 2,3,5,6-1H,4H-tetrahydro-8-methylquinolizino-<9,9a,1-gh>coumarin; 2,3,5,6-1H,4H-tetrahydro-9-(3-pyridyl)-quinolizino-<9,9a,1-gh>coumarin; 2,3,5,6-1H,4H-tetrahydro-8-trifluoromethylquinolizino-<9,9a,1-gh>coumarin; 3,3',2''',3'''-tetramethyl-p-quaterphenyl; 32
2,5,2',5'-tetramethyl-p-quinquephenyl; P-terphenyl; P-quaterphenyl; nile red; rhodamine 700; oxazine 750; rhodamine 800; IR 125; IR 144; IR 140; IR 132; IR 26; IR5; diphenylhexatriene; diphenylbutadiene; tetraphenylbutadiene; naphthalene; anthracene; 9,10-diphenylanthracene; pyrene; chrysene; rubrene; coronene; phenanthrene and the like, and combinations comprising at least one of the foregoing dyes. Dyes are generally used in amounts of about 0.1 parts per million to about 10 parts by weight, based on 100 parts by weight of parts by weight of the polycarbonate component and the impact modifier composition.

Monomeric, oligomeric, or polymeric antistatic additives that may be sprayed onto the article or processed into the thermoplastic composition may be advantageously used. Examples of monomeric antistatic agents include long chain esters such as glycerol monostearate, glycerol distearate, glycerol tristearate, and the like, sorbitan esters, and ethoxylated alcohols, alkyl sulfates, alkylarylsulfates, alkylphosphates, alkylaminesulfates, alkyl sulfonate salts such as sodium stearyl sulfonate, sodium dodecylbenzenesulfonate and the like, fluorinated alkylsulfonate salts, betaines, and the like. Combinations of the foregoing antistatic agents may be used. Exemplary polymeric antistatic agents include certain polyetheresters, each containing polyalkylene glycol moieties such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and the like. Such polymeric antistatic agents are commercially available, and include, for example PELESTAT 6321 (Sanyo), PEBAX MH1657 (Atofina), and IRGASTAT P18 and P22 (Ciba-Geigy). Other polymeric materials that may be used as antistatic agents are inherently conducting polymers such as polythiophene (commercially available from Bayer), which retains some of its intrinsic conductivity after melt processing at elevated temperatures. In one embodiment, carbon fibers, carbon nanofibers, carbon nanotubes, carbon black or any combination of the foregoing may be used in a polymeric resin containing chemical antistatic agents to render the composition electrostatically dissipative. Antistatic agents are generally used in amounts of about 0.1 to about 10 parts by weight, specifically about based on 100 parts by weight of the polycarbonate component and the impact modifier composition.
Where a foam is desired, suitable blowing agents include, for example, low boiling halohydrocarbons and those that generate carbon dioxide; blowing agents that are solid at room temperature and when heated to temperatures higher than their decomposition temperature, generate gases such as nitrogen, carbon dioxide ammonia gas, such as azodicarbonamide, metal salts of azodicarbonamide, 4,4'-oxybis(benzenesulfonylhydrazide), sodium bicarbonate, ammonium carbonate, and the like, or combinations comprising at least one of the foregoing blowing agents. Blowing agents are generally used in amounts of about 0.5 to about 20 parts by weight, based on 100 parts by weight of polycarbonate component and the impact modifier composition.

Suitable flame retardant that may be added are stable, specifically hydrolytically stable. A hydrolytically stable flame retardant does not substantially degrade under conditions of manufacture and/or use to generate species that can catalyze or otherwise contribute to the degradation of the polycarbonate composition. Such flame retardants may be organic compounds that include phosphorus, bromine, and/or chlorine. The polysiloxane-polycarbonate copolymers described above may also be used. Non-brominated and non-chlorinated phosphorus-containing flame retardants may be preferred in certain applications for regulatory reasons, for example certain organic phosphates and/or organic compounds containing phosphorus-nitrogen bonds.

One type of exemplary organic phosphate is an aromatic phosphate of the formula (GO)₃P=O, wherein each G is independently an alkyl, cycloalkyl, aryl, alkaryl, or aralkyl group, provided that at least one G is an aromatic group. Two of the G groups may be joined together to provide a cyclic group, for example, diphenyl pentacrythritol diphosphate, which is described by Axelrod in U.S. Pat. No. 4,154,775. Other suitable aromatic phosphates may be, for example, phenyl bis(dodecyl) phosphate, phenyl bis(neopentyl) phosphate, phenyl bis(3,5,5'-trimethylhexyl) phosphate, ethyl diphenyl phosphate, 2-ethylhexyl di(p-tolyl) phosphate, bis(2-ethylhexyl) p-toly phosphate, tritolyl phosphate, bis(2-ethylhexyl) phenyl phosphate, tri(nonylphenyl) phosphate, bis(dodecyl) p-toly phosphate, dibutyl phenyl phosphate, 2-chloroethyl diphenyl phosphate, p-toly bis(2,5,5'-trimethylhexyl) phosphate, 2-ethylhexyl diphenyl phosphate, and the like. A specific aromatic
phosphate is one in which each $G$ is aromatic, for example, triphenyl phosphate, tricresyl phosphate, isopropylated triphenyl phosphate, and the like.

Di- or polyfunctional aromatic phosphorus-containing compounds are also useful, for example, compounds of the formulas below:

\[
\begin{align*}
&\text{\[G^1\text{O-P-}[\text{\begin{array}{c}
\text{O-X}^m
\text{O-P-}[\text{\begin{array}{c}
\text{O-X}^m
\text{OG}^1
\end{array}]_n
\end{array}]_n
\end{align*}}
\]
\[
\begin{align*}
&\text{\[G^1\text{O-P-}[\text{\begin{array}{c}
\text{O-X}^m
\text{O-P-}[\text{\begin{array}{c}
\text{O-X}^m
\text{OG}^1
\end{array}]_n
\end{array}]_n
\end{align*}}
\]
\]

wherein each $G^1$ is independently a hydrocarbon having 1 to about 30 carbon atoms; each $G^2$ is independently a hydrocarbon or hydrocarbonyl having 1 to about 30 carbon atoms; each $X$ is independently a bromine or chlorine; $m$ is 0 to 4, and $n$ is 1 to about 30. Examples of suitable di- or polyfunctional aromatic phosphorus-containing compounds include resorcinol tetrphenyl diphosphate (RDP), the bis(diphenyl) phosphate of hydroquinone and the bis(diphenyl) phosphate of bisphenol-A, respectively, their oligomeric and polymeric counterparts, and the like.

Exemplary suitable flame retardant compounds containing phosphorus-nitrogen bonds include phosphonitrilic chloride and tris(aziridinyl) phosphine oxide. When present, phosphorus-containing flame retardants are generally present in amounts of about 1 to about 20 parts by weight, based on 100 parts by weight of polycarbonate component and the impact modifier composition.

Halogenated materials may also be used as flame retardants, for example halogenated compounds and resins of the formula (11):
\[
\left( Y \right)_d \left( X \right)_c \left( Y \right)_d \\
\text{Ar} \quad \text{R} \quad \text{Ar'} \quad c
\]

(11)

wherein \( R \) is an alkylene, alkylidene or cycloaliphatic linkage, e.g., methylene, propylene, isopropylidene, cyclohexylene, cyclopentidene, and the like; an oxygen ether, carbonyl, amine, or a sulfur containing linkage, e.g., sulfide, sulfoxide, sulfone, and the like; or two or more alkylene or alkylidene linkages connected by such groups as aromatic, amino, ether, carbonyl, sulfide, sulfoxide, sulfone, and the like groups; \( \text{Ar} \) and \( \text{Ar'} \) are each independently a mono- or polycarboxyclic aromatic group such as phenylene, biphenylene, terphenylene, naphthylene, and the like, wherein hydroxyl and \( Y \) substituents on \( \text{Ar} \) and \( \text{Ar'} \) can be varied in the ortho, meta or para positions on the aromatic rings and the groups can be in any possible geometric relationship with respect to one another; each \( Y \) is independently an organic, inorganic or organometallic radical, for example (1) a halogen such as chlorine, bromine, iodine, or fluorine, (2) an ether group of the general formula \(-\text{OE}\), wherein \( \text{E} \) is a monovalent hydrocarbon radical similar to \( X \), (3) monovalent hydrocarbon groups of the type represented by \( R \) or (4) other substituents, e.g., nitro, cyano, and the like, said substituents being essentially inert provided there be at least one and preferably two halogen atoms per aryl nucleus; each \( X \) is independently a monovalent \( C_{1-18} \) hydrocarbon group such as methyl, propyl, isopropyl, decyl, phenyl, naphthyl, biphenyl, xylyl, tollyl, benzyl, ethylphenyl, cyclopentyl, cyclohexyl, and the like, each optionally containing inert substituents; each \( d \) is independently 1 to a maximum equivalent to the number of replaceable hydrogens substituted on the aromatic rings comprising \( \text{Ar} \) or \( \text{Ar'} \); each \( e \) is independently 0 to a maximum equivalent to the number of replaceable hydrogens on \( R \); and each \( a, b, \) and \( c \) is independently a whole number, including 0, with the proviso that when \( b \) is 0, either \( a \) or \( c \), but not both, may be 0, and when \( b \) is not 0, neither \( a \) nor \( c \) may be 0.

Included within the scope of the above formula are bisphenols of which the following are representative: bis(2,6-dibromophenyl)methane; 1,1-bis(4-iodophenyl)ethane; 2,6-bis(4,6-dichloronaphthyl)propane; 2,2-bis(2,6-dichlorophenyl)pentane; bis(4-hydroxy-2,6-dichloro-3-methoxyphenyl)methane; and 2,2-bis(3-bromo-4-
hydroxyphenyl)propane. Also included within the above structural formula are 1,3-
dichlorobenzene, 1,4-dibromobenzene, and biphenyls such as 2,2'-dichlorobiphenyl,
polybrominated 1,4-diphenoxypbenzene, 2,4'-dibromobiphenyl, and 2,4'-
dichlorobiphenyl as well as decabromo diphenyl oxide, and the like. Also useful are
oligomeric and polymeric halogenated aromatic compounds, such as a
copolycarbonate of bisphenol A and tetrabromobisphenol A and a carbonate
precursor, e.g., phosgene. Metal synergists, e.g., antimony oxide, may also be used
with the flame retardant. When present, halogen containing flame retardants are
generally used in amounts of about 1 to about 50 parts by weight, based on 100 parts
by weight of the polycarbonate component and the impact modifier composition.

Another useful type of flame retardant is a polysiloxane-polycarbonate copolymer
having polydiorganosiloxane blocks comprise repeating structural units of formula
(12):

![Chemical structure diagram](image)

(12)

wherein each occurrence of R is same or different, and is a C1-13 monovalent organic
radical. For example, R may be a C1-C13 alkyl group, C1-C13 alkoxy group, C2-C13
alkenyl group, C2-C13 alkenyloxy group, C3-C6 cycloalkyl group, C3-C6 cycloalkoxy
group, C6-C10 aryl group, C6-C10 aryloxy group, C7-C13 aralkyl group, C7-C13
aralkoxy group, C7-C13 alkaryl group, or C7-C13 alkaryloxy group. Combinations of
the foregoing R groups may be used in the same copolymer. R2 in formula (6) is a
divalent C1-C8 aliphatic group. Each M in formula (7) may be the same or different,
and may be a halogen, cyano, nitro, C1-C8 alkylthio, C1-C8 alkyl, C1-C8 alkoxy, C2-C8
alkenyl, C2-C8 alkenyloxy group, C3-C8 cycloalkyl, C3-C8 cycloalkoxy, C6-C10 aryl,
C6-C10 aryloxy, C7-C12 aralkyl, C7-C12 aralkoxy, C7-C12 alkaryl, or C7-C12 alkaryloxy,
wherein each n is independently 0, 1, 2, 3, or 4.

D in formula (6) is selected so as to provide an effective level of flame retardance to
the polycarbonate composition. The value of D will therefore vary depending on the
relative amount of each component in the polycarbonate composition, including the amount of polycarbonate, impact modifier, polysiloxane-polycarbonate copolymer, and other flame retardants. Suitable values for D may be determined by one of ordinary skill in the art without undue experimentation using the guidelines taught herein. Generally, D has an average value of 10 to about 250, specifically about 10 to about 60.

In one embodiment, M is independently bromo or chloro, a C_1-C_3 alkyl group such as methyl, ethyl, or propyl, a C_1-C_3 alkoxy group such as methoxy, ethoxy, or propoxy, or a C_2-C_7 aryl group such as phenyl, chlorophenyl, or tolyl; R^2 is a dimethylene, trimethylene or tetramethylene group; and R is a C_1-C_8 alkyl, haloalkyl such as trifluoropropyl, cyanoalkyl, or aryl such as phenyl, chlorophenyl or tolyl. In another embodiment, R is methyl, or a mixture of methyl and trifluoropropyl, or a mixture of methyl and phenyl. In still another embodiment, M is methoxy, n is one, R^2 is a divalent C_1-C_3 aliphatic group, and R is methyl.

The polysiloxane-polycarbonate copolymer may be manufactured by reaction of the corresponding dihydroxy polysiloxane with a carbonate source and a dihydroxy aromatic compound of formula (3), as described above for polycarbonates. Generally, the amount of dihydroxy polydiorganosiloxane is selected so as to produce a copolymer comprising about 1 to about 60 mole percent of polydiorganosiloxane blocks relative to the moles of polycarbonate blocks, and more generally, about 3 to about 50 mole percent of polydiorganosiloxane blocks relative to the moles of polycarbonate blocks. When present, the copolymers may be used in amounts of about 5 to about 50 parts by weight, more specifically about 10 to about 40 parts by weight, based on 100 parts by weight of polycarbonate component and the impact modifier composition.

Inorganic flame retardants may also be used, for example salts of C_2-C_6 alkyl sulfonates such as potassium perfluorobutane sulfonate (Rimar salt), potassium perfluoro-octane sulfonate, tetraethylammonium perfluorohexane sulfonate, and potassium diphenyl sulfone sulfonate; salts such as CaCO_3, BaCO_3, and BaCrO_3; salts of fluoro-anion complex such as Li_3AlF_6, BaSiF_6, KBF_4, K_3AlF_6, KAI_F_4, K_2SiF_6, and
Na$_3$AlF$_6$; and the like. When present, inorganic flame retardant salts are generally present in amounts of about 0.01 to about 25 parts by weight, more specifically about 0.1 to about 10 parts by weight, based on 100 parts by weight of the polycarbonate component and the impact modifier composition.

Anti-drip agents may also be used, for example a fibril forming or non-fibril forming fluoropolymer such as polytetrafluoroethylene (PTFE). The anti-drip agent may be encapsulated by a rigid copolymer as described above, for example SAN. PTFE encapsulated in SAN is known as TSAN. Encapsulated fluoropolymers may be made by polymerizing the encapsulating polymer in the presence of the fluoropolymer, for example an aqueous dispersion. TSAN may provide significant advantages over PTFE, in that TSAN may be more readily dispersed in the composition. A suitable TSAN may comprise, for example, about 50 wt.% PTFE and about 50 wt.% SAN, based on the total weight of the encapsulated fluoropolymer. The SAN may comprise, for example, about 75 wt.% styrene and about 25 wt.% acrylonitrile based on the total weight of the copolymer. Alternatively, the fluoropolymer may be pre-blended in some manner with a second polymer, such as for, example, an aromatic polycarbonate resin or SAN to form an agglomerated material for use as an anti-drip agent. Either method may be used to produce an encapsulated fluoropolymer. Antidrip agents are generally used in amounts of about 0.1 to about 10 parts by weight, based on 100 parts by weight of polycarbonate component and the impact modifier composition.

The thermoplastic compositions may be manufactured by methods generally available in the art, for example, in one embodiment, in one manner of proceeding, powdered polycarbonate, other resin if used, impact modifier composition, and/or other optional components are first blended, optionally with chopped glass strands or other fillers in a Henschel high speed mixer. Other low shear processes including but not limited to hand mixing may also accomplish this blending. The blend is then fed into the throat of a twin-screw extruder via a hopper. Alternatively, one or more of the components may be incorporated into the composition by feeding directly into the extruder at the throat and/or downstream through a sidestuffer. Such additives may also be compounded into a masterbatch with a desired polymeric resin and fed into the
extruder. The additives may be added to either the polycarbonate base materials or the ABS base material to make a concentrate, before this is added to the final product. The extruder is generally operated at a temperature higher than that necessary to cause the composition to flow, typically 500°F (260°C) to 650°F (343 °C). The extrudate is immediately quenched in a water bath and pelletized. The pellets, so prepared, when cutting the extrudate may be one-fourth inch long or less as desired. Such pellets may be used for subsequent molding, shaping, or forming.

Shaped, formed, or molded articles comprising the thermoplastic compositions are also provided. The thermoplastic compositions may be molded into useful shaped articles by a variety of means such as injection molding, extrusion, rotational molding, blow molding and thermoforming to form articles such as, for example, computer and business machine housings such as housings for monitors, handheld electronic device housings such as housings for cell phones, electrical connectors, and components of lighting fixtures, ornaments, home appliances, roofs, greenhouses, sun rooms, swimming pool enclosures, and the like.

The compositions find particular utility in automotive applications, for example interior parts such as instrument panels, overhead consoles, interior trim, center consoles, and the like; and exterior parts such as body panels, exterior trim, bumpers, and the like.

The thermoplastic compositions described herein have significantly improved hydrolytic aging stability. In a particularly advantageous feature, the thermoplastic compositions may achieve improved hydrolytic aging stability without significant degradation in thermal aging stability. Certain embodiments may further achieve improved hydrolytic aging stability without significant degradation in thermal aging stability and impact strength.

The thermoplastic compositions have significantly improved hydrolytic aging stability as reflected by a reduction in percent change in melt flow rate (MFR) after exposure to high humidity and/or high temperature conditions. MFR is the rate of extrusion of thermoplastics through an orifice at a prescribed temperature and load, and may be
measured in accordance with ISO 1133 or ASTM D1238. It provides a means of measuring flow of a melted material, which can be used to determine the extent of degradation of the thermoplastic as a result of exposure to heat and/or humidity. Degraded materials would generally flow more as a result of reduced molecular weight, and could exhibit reduced physical properties. Typically, flow rates are determined before and after storage under conditions of high humidity, then a percentage difference is calculated.

Thus, in one embodiment, the change in MFR measured at 260°C, 5 kilogram (Kg) (after six minutes of preheating) is less than about 60%, specifically less than about 50%, more specifically less than about 40%, and more specifically less than about 30% of the initial MFR value after exposure to an environment of 90°C / 95% relative humidity (RH) for 1000 hours. In another embodiment, these compositions may also have a change in MFR measured at 260°C, 5 Kg (after six minutes of preheating), of less than about 50%, specifically less than about 40%, more specifically less than about 30%, and more specifically less than about 20% of the initial MFR value after exposure to an environment of 110°C for 1000 hours at ambient humidity (generally 1-2% humidity).

In another embodiment, the thermoplastic compositions may have significantly improved hydrolytic aging stability as reflected by a decreased reduction in molecular weight after exposure to high humidity conditions. Molecular weight is measured by GPC (gel permeation chromatography) in methylene chloride solvent. Polystyrene calibration standards are used to determine relative molecular weights. Changes in weight average molecular weight are typically used. This provides a means of measuring changes in chain length of a polymeric material, which can be used to determine the extent of degradation of the thermoplastic as a result of exposure to heat and/or humidity. Degraded materials would generally show reduced molecular weight, and could exhibit reduced physical properties. Typically, molecular weights are determined before and after storage under conditions of high humidity, then a percentage difference is calculated.
Thus, in one embodiment, the change in weight average molecular weight measured by GPC in dichloromethane using polystyrene standards is less than about 60%, specifically less than about 50%, more specifically less than about 40%, and more specifically less than about 30% of the initial value after exposure to an environment of 90°C / 95% relative humidity (RH) for 1000 hours. In another embodiment, the change in weight average molecular weight measured by GPC in dichloromethane using polystyrene standards is less than about 60%, specifically less than about 50%, more specifically less than about 40%, and more specifically less than about 30% of the initial value after exposure to an environment of 110°C for 1000 hours at ambient humidity for 1000 hours.

In another embodiment, the thermoplastic compositions may have significantly improved hydrolytic aging stability as reflected by a smaller increase in melt viscosity (MV) after exposure to high humidity conditions. Melt viscosity is a measure of a polymer at a given temperature at which the molecular chains can move relative to each other. Melt viscosity is dependent on the molecular weight, in that the higher the molecular weight, the greater the entanglements and the greater the melt viscosity, and can therefore be used to determine the extent of degradation of the thermoplastic as a result of exposure to heat and/or humidity. Degraded materials would generally show increased viscosity, and could exhibit reduced physical properties. Melt viscosity is determined against different shear rates, and may be conveniently determined by DIN 54811. Typically, melt viscosities are determined before and after storage under conditions of high humidity, then a percentage difference is calculated.

Thus, in one embodiment, the change in MV measured at 260°C at shear rates of 100, 500, 1000, 1500, 5000, and 10,000 s⁻¹ is less than about 60%, specifically less than about 50%, more specifically less than about 40%, more specifically less than about 30%, and even more specifically less than about 20% of the initial MV value after exposure to an environment of 90°C / 95% relative humidity (RH) for 1000 hours. In another embodiment, the change in MV is less than about 60%, specifically less than about 50%, more specifically less than about 40%, more specifically less than about 30%, and even more specifically less than about 20% of the initial value after
exposure to an environment of 110°C for 1000 hours at ambient humidity for 1000 hours.

The compositions described herein may further have excellent physical properties and good processability. For example, the thermoplastic polycarbonate compositions may have a heat deflection temperature (HDT) of about 80 to about 120°C, more specifically about 100 to about 110°C, measured at 1.8 MPa on a 4 mm thick bar according to ISO 75Ae.

The thermoplastic polycarbonate compositions may further have a low temperature notched Izod Impact of greater than about 25 KJ/m², specifically greater than about 35 KJ/m², determined at −30°C using a 4 mm thick bar per ISO 180/1A.

The thermoplastic polycarbonate compositions may further have a Charpy Impact of about 25 KJ/m² determined at −30°C, more specifically about 35 KJ/m², determined at −30°C, determined using a 4 mm thick per ISO 179/1eA.

The thermoplastic polycarbonate compositions may further have a Vicat B/50 of about 120 to about 140°C, more specifically about 126 to about 132°C, determined using a 4 mm thick bar per ISO 306.

The thermoplastic polycarbonate compositions may further have a Instrumented Impact Energy (dart impact) at maximum load of at least about 20, preferably at least about 30 ft-lb, determined using a 4-inch (10 cm) diameter disk at −30°C, ½-inch (12.7 mm) diameter dart, and an impact velocity of 6.6 meters per second (m/s) per ASTM D3763.

In another surprising feature, it has been found that carbon and/or VOC (volatile organic chemical) emissions from the compositions are lowered. Low VOC emissions are desirable in applications such as interior automobile parts, as they result in less fogging. The compositions furthermore have less odor. Carbon emissions from the samples may be determined in accordance with PV 3341. Carbon emissions may be less than about 30, specifically less than about 25, more specifically less than about 20 micrograms of carbon per gram of composition. FOG and VOC emissions
may be determined in accordance with VDA 278 using a sample treatment of 80°C for two hours, which is standard for large automotive interior parts. VOC emissions may be less than about 10 ppm, specifically about 0.1 to about 6 ppm, and more specifically about 3 to about 4 ppm. FOG may be below about 5 ppm, about 0.1 about 3 ppm, and more specifically about 0.5 to about 1 ppm. Odor is may be below about 4, specifically about 1 to about 3.

The invention is further illustrated by the following non-limiting Examples.

In the examples, the polycarbonates (PC) are based on Bisphenol A, and have a molecular weight of 10,000 to 120,000, more specifically 18,000 to 40,000 (on an absolute molecular weight scale), available from GE Advanced Materials under the trade name LEXAN. The initial melt flow of the polycarbonates was about 6 to about 27 measured at 300°C using a 1.2 Kg load, per ASTM D1238.

The MBS is Rohm & Haas EXL2691A (powder) or Rohm & Haas EXL3691A (pelletized), nominal 75 - 82 wt.% butadiene core with a balance styrene-methyl methacrylate shell. The MBS is preferably manufactured in accordance with the process described U.S. Pat. No. 6,545,089, and is substantially free of impurities, residual acids, residual bases or residual metals that may catalyze the hydrolysis of polycarbonate. Control of the manufacture of the MBS to provide a slurry of the MBS having a pH of about 6 to about 7 provides optimal hydrolytic stability. The pH of a slurry of each of the components is measured using 1 g of the component and 10 mL of distilled water having a pH of 7 and containing a drop of isopropyl alcohol as a wetting agent.

The SAN used is a bulk process material having an acrylonitrile content of 25 wt.%.

The bulk ABS (BABS) had a nominal 15 wt.% butadiene and a nominal 15 wt.% acrylonitrile content. The microstructure is phased inverted, with occluded SAN in a butadiene phase in a SAN matrix. The BABS was manufactured using a plug flow reactor in series with a stirred, boiling reactor as described, for example, in U.S. Patent No. 3,981,944 and U.S. Patent No. 5,414,045.
Samples without steam stripping were prepared by melt extrusion on a Werner & Pfleider 30 mm twin screw extruder, using a nominal melt temperature of 525°F (274°C), 25 inches (635 mm) of mercury vacuum, and 500 rpm. The extrudate was pelletized and dried at about 120°C for about 4 hours. Samples with steam stripping were prepared by melt extrusion on a Werner & Pfleider 25 mm twin screw extruder using steam stripped designed screws, a nominal melt temperature of 260°C, 25 inches (635 mm) of mercury vacuum, and 450 rpm. The extrudate was pelletized and dried at about 120°C for about 2 hours.

To make test specimens, the dried pellets were injection molded on an 85-ton injection molding machine at a nominal temp of 525°C, wherein the barrel temperature of the injection molding machine varied from about 285°C to about 300°C. Specimens were tested in accordance with ASTM or ISO standards as described above.

Table 1 below shows the predicted percent change in melt flow after hydrolytic aging at 90°C/95% RH for 500 and 1000 hours, as well as thermal aging at 110°C for 500 and 1000 hours. Comparative examples A and B are illustrative of conventional PC/ABS systems using an emulsion polymerized ABS, and contain no MBS. Comparative example C is illustrative of a conventional PC/ABS system using a stabilizer composition optimized for improved hydrolytic stability, and contains no MBS. Example D, which is in accordance with the present invention, comprises 70 wt.% PC, 21.5 wt.% BABS, and 8.5 wt.% MBS, plus stabilizers and mold release agents as are known in the art. The values reported in this Table represent model predictions from a design space in which these compositions were systematically varied. The model used was a D-Optimal Crossed Mixture design developed using the Design Expert 6.01 Experimental design program. The program used the data given in the table below, with numerical optimization selected for minimal melt flow shift under all aging conditions.

Table 1
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<tr>
<td></td>
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</tr>
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</tr>
<tr>
<td>D</td>
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*Comparative

The above results illustrate that compositions in accordance with the present invention exhibit significant improvement in the percent change in melt flow before and after hydrolytic aging at 90°C/95% RH for 500 and 1000 hours, as well as thermal aging at 110°C for 500 and 1000 hours.

Examples 1-23 shown in Table 2 below are in accordance with the present invention, and Examples 24-37 are comparative. Comparative Examples 33-37 are illustrative of conventional PC/ABS systems using an emulsion polymerized ABS, and contain no MBS. Properties of these examples are shown in Table 2. “DMFR” is the change in melt flow rate after aging at 90°C/95% RH, measured at 260°C using a 5 Kg load after preheating for six minutes per ASTM D1238.
### Table 2

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<th>Ex. No.</th>
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<th>BABS, wt.%</th>
<th>MBS, wt.%</th>
<th>PC MW, Kg/mole</th>
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<th>Dyn E&lt;sub&gt;max&lt;/sub&gt; at -30°C, ft-lbs after aging</th>
<th>Izod at -30°C, % ductile after aging</th>
<th>E&lt;sub&gt;max&lt;/sub&gt; at -30°C, kJ/m² after aging</th>
<th>DMFR, % change after aging</th>
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*a Polycarbonate synthesized using an interfacial process

*b Polycarbonate synthesized using a melt process

*Example was steam stripped to remove volatiles by steam injection into the melt in the extruder, before the vacuum vent.

The above results clearly show better melt stability for the compositions of the present invention upon exposure to conditions of high heat and humidity, as evidenced by the reduction in percent change in the melt volume index before and after aging. In particular, the instant examples show a percent change in viscosity of about 13 to about 31%, whereas the comparative examples show a percent change in viscosity from 53 to 2084%.

As used herein, “(meth)acrylate” is inclusive of both acrylates and methacrylates. Further as used herein, the terms “first,” “second,” and the like do not denote any order or importance, but rather are used to distinguish one element from another, and the terms “the”, “a” and “an” do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item. All ranges disclosed herein for the same properties or amounts are inclusive of the endpoints, and each of the endpoints is independently combinable. All cited patents, patent applications, and other references are incorporated herein by reference in their entirety.

While the invention has been described with reference to a preferred embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope
of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.

What is claimed is:
What is claimed is:

1. A thermoplastic composition comprising in combination

   a polycarbonate component; and

   an impact modifier composition wherein the components of the impact modifier
   composition are substantially free of a species that degrades a polycarbonate, the
   components comprising

   a bulk polymerized ABS; and

   an impact modifier different from the ABS.

2. The composition of claim 1 wherein a slurry of each of the individual
   components of the impact modifier composition have a pH of about 3 to about 8.

3. The composition of claim 1 further comprising an additive, wherein a slurry of
   each of the individual additives has a pH of about 4 to about 7.

4. The composition of claim 1 further comprising an additive, wherein a slurry of
   each of the individual additives has a pH of about 6 to about 7.

5. The composition of claim 1, comprising 1 to about 95 wt.% polycarbonate,
   about 5 to about 98 wt.% bulk polymerized ABS, about 1 to about 95 wt.% impact
   modifier different from ABS, and up to about 50 wt.% of a rigid copolymer, wherein
   each of the foregoing amounts is based on the total weight of the polycarbonate, bulk
   polymerized ABS, impact modifier different from ABS, and any rigid copolymer.

6. The composition of claim 1, comprising about 20 to about 84 wt.%
   polycarbonate, about 5 to about 50 wt.% bulk polymerized ABS, about 4 to about 20
   wt.% impact modifier different from ABS, and 1 to about 20 wt.% of a rigid
   copolymer, wherein each of the foregoing amounts is based on the total weight of the
   polycarbonate, bulk polymerized ABS, impact modifier different from ABS, and rigid
   copolymer.

7. The composition of claim 1, comprising about 64 to about 74 wt.%
   polycarbonate, about 5 to about 35 wt.% bulk polymerized ABS, about 2 to about 10
wt.% impact modifier different from ABS, and about 2 to about 8 wt.% of a rigid copolymer, wherein each of the foregoing amounts is based on the total weight of the polycarbonate, bulk polymerized ABS, impact modifier different from ABS, and rigid copolymer.

8. The composition of claim 1 wherein the impact modifier other than bulk polymerized ABS is prepared by emulsion polymerization.

9. The composition of claim 8 wherein the emulsion polymerization is conducted in the absence of a species that degrades a polycarbonate.

10. The composition of claim 8 wherein the emulsion polymerization is conducted in the absence of a basic species.

11. The composition of claim 8 wherein the impact modifier other than bulk polymerized ABS is prepared by emulsion polymerization using a C_{1-22} alkyl sulfonate, a C_{7-25} alkylaryl sulfonate, a C_{1-22} alkyl sulfate, a C_{7-25} alkylaryl sulfate, a C_{1-22} alkyl phosphate, a C_{7-25} alkylaryl phosphate, a substituted silicates, or a combination comprising at least one of the foregoing surfactants.

12. The composition of claim 8 wherein the impact modifier other than bulk polymerized ABS comprises an elastomeric phase comprising a butadiene rubber, an isoprene rubber, an ethylene-propylene rubber, an ethylene-propylene-diene monomer rubber, an ethylene-vinyl acetate rubbers, a silicone rubber, an elastomeric rubber derived from a C_{4,8} alkyl (meth)acrylate; an elastomeric copolymer of a C_{1,4} alkyl (meth)acrylate with butadiene and/or styrene, or a combination comprising at least one of the foregoing elastomers, together with a rigid copolymer phase derived from the copolymerization of a monomer of formula (9):

![Chemical Structure](image)

(9)
wherein each $X^e$ is independently hydrogen, C$_1$-C$_{12}$ alkyl, C$_3$-C$_{12}$ cycloalkyl, C$_6$-C$_{12}$ aryl, C$_7$-C$_{12}$ aralkyl, C$_7$-C$_{12}$ alkaryl, C$_1$-C$_{12}$ alkoxy, C$_3$-C$_{12}$ cycloalkoxy, C$_6$-C$_{12}$ aryloxy, chloro, bromo, or hydroxy, and $R$ is hydrogen, C$_1$-C$_5$ alkyl, bromo, or chloro, with a monomer of the generic formula (10):

![Generic formula (10)](image)

wherein $R$ is hydrogen, C$_1$-C$_5$ alkyl, bromo, or chloro, and $X^e$ is cyano, C$_1$-C$_{12}$ alkoxy carbonyl, C$_1$-C$_{12}$ aryloxy carbonyl, or hydroxycarbonyl.

13. The composition of claim 8 wherein the elastomer phase comprises polybutadiene and the rigid copolymer phase comprises units derived from the copolymerization of styrene, alpha-methyl styrene, dibromostyrene, vinyltoluene, vinylxylene, butylstyrene, para-hydroxystyrene, methoxystyrene, or a combination comprising at least one of the foregoing styrenes with acrylonitrile, ethacrylonitrile, methacrylonitrile, alpha-chloroacrylonitrile, beta-chloroacrylonitrile, alpha-bromoacrylonitrile, acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, t-butyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, or a combination comprising at least one of the foregoing co-monomers.

14. The composition of claim 1 wherein the impact modifier other than bulk polymerized ABS is MBS, AES, MABS, ASA, or a combination comprising at least one of the foregoing impact modifiers.

15. The composition of claim 1 further comprising an additive substantially free of a species that degrades a polycarbonate and/or that is treated to prevent degradation of the polycarbonate.

16. The composition of claim 15 wherein the additive is a filler, a reinforcing agent, a pigment, or a combination comprising at least one of the foregoing additives.

17. The composition of claim 16 wherein the treatment is by coating and/or chemical passivation.
18. The composition of claim 1, having a percent change in melt flow rate after aging at 90°C/95% RH of less than about 60%, wherein the melt flow is measured at 260°C using a 5 Kg load after preheating for six minutes per ASTM D1238.

19. The composition of claim 1, having a percent change in melt flow rate after aging at 110°C/2% RH of less than about 60%, wherein the melt flow is measured at 260°C using a 5 Kg load after preheating for six minutes per ASTM D1238.

20. The composition of claim 1, having a notched Izod impact strength of greater than about greater than about 25 KJ/m², determined at −30°C using a 4 mm thick bar per ISO 180/1A.

21. The composition of claim 1, having a percent change in weight average molecular weight rate after aging at 90°C/95% RH of less than about 60%, wherein the weight average molecular weight is measured by gel permeation chromatography in dichloromethane using polystyrene standards.

22. The composition of claim 1, having a percent change in weight average molecular weight rate after aging at 90°C/95% RH of less than about 20%, wherein the weight average molecular weight is measured by gel permeation chromatography in dichloromethane using polystyrene standards.

23. The composition of claim 1, having a percent change in melt viscosity rate after aging at 90°C/95% RH of less than about 60%, wherein the melt viscosity is measured at 260°C using shear rates of 100, 500, 1000, 1500, 5000, and 10,000 s⁻¹ per DIN 54811.

24. An article comprising the composition of claim 1.

25. The article of claim 24, in the form of an automobile component.

26. The article of claim 24, further comprising a colorant substantially free of a species that degrades a polycarbonate and/or that is treated to prevent degradation of the polycarbonate.
27. A method of manufacture of an article comprising molding, extruding, or shaping the composition of claim 1.

28. The method of claim 27, wherein an additive is combined with a polycarbonate, a bulk polymerized ABS, an impact modifier different from the ABS, a rigid copolymer, or a combination comprising at least one of the foregoing; and the combined additive is added to the thermoplastic composition during molding, extruding, or shaping.

29. An article made by the method of claim 27.

30. A method for the manufacture of a thermoplastic composition having improved hydrolytic and/or thermal stability, the method comprising admixture of a polycarbonate, a bulk polymerized ABS, and an impact modifier different from the ABS, wherein each component of the composition is essentially free from a species that degrades the polycarbonate.


32. An article made from the thermoplastic composition of claim 31.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
COBL69/00

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)
CO8L

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 practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X Further documents are listed in the continuation of box C. X Patent family members are listed in 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 document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *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

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principles or theory underlying the invention

*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.

"A' document: member of the same patent family

Date of the actual completion of the international search
23 November 2005

Date of mailing of the international search report
29/11/2005

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European Patent Office, P.B. 5818 Patentlaan 2
ML - 2280 HV RIJKEN
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Fax: (+31-70) 340-3016

Authorized officer
Lohner, P
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