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(54) Title: IMPACT RESISTANT BLENDS OF HIGH HEAT POLYCARBONATE AND AROMATIC POLYESTER

(57) Abstract

A composition possessing a desirably high balance of resistance to thermal deformation and to chemical solvents, and reduced notch sensitivity, prepared from a polycarbonate having a glass transition temperature in excess of at least 165 °C, an aromatic polyester, a polyphenylene ether, and an elastomeric impact modifier such as a thermoplastic elastomer, a core-shell grafted copolymer or an olefinic elastomer.

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Impact Resistant Blends of High Heat Polycarbonate and Aromatic Polyester

This invention relates to carbonate polymers, particularly those which have good resistance to thermal deformation, and to compositions formed therefrom.

Polycarbonate is a useful engineering thermoplastic because it possesses, in general, a combination of several different favorable properties. Certain polycarbonates which have a glass transition temperature exceeding at least 165°C, known as "high heat" polycarbonates, additionally have better resistance to thermal deformation than others. However, it is often found that a high heat polycarbonate is notch sensitive to impact loading, and often is undesirably subject to failure by brittle fracture. Brittle fracture, in this context, is usually indicated when a point of applied stress where fracture occurs exhibits smooth fracture surfaces, does not exhibit shear lips, and is not hinged. As a consequence of its brittleness, a high heat polycarbonate typically exhibits a low level of toughness, manifested particularly as notch sensitivity to impact loading, at a sufficiently high level to outweigh the benefits which would otherwise be obtainable from its superior resistance to thermal deformation.

When a blend is formed from polyester and a polycarbonate which has a T_g of 150°C or less, the brittleness which would be present in the resulting blend because of the presence of the polyester can be more readily offset by the addition of an elastomer because the matrix provided by a polycarbonate which does not possess exceptionally high thermal resistance is ductile in and of itself. Experience with such varieties of ductile polycarbonate does not therefore furnish any guidance concerning reducing the brittleness of a high heat polycarbonate.

Polyester tends to be a brittle, notch-sensitive material itself, and even an elastomeric impact modifier is not always adequate to significantly reduce the inherent brittleness of a blend of polyester with a high heat polycarbonate. Moreover, regardless of the system selected to reduce the notch sensitivity to impact loading of a high heat polycarbonate composition, the high viscosity inherent in a high heat polycarbonate requires that, in preparation of a composition, a high heat polycarbonate be selected which will allow for easy and convenient processing on known types of equipment.

It would accordingly be desirable if, by employing appropriate methods and materials, the notch sensitivity to impact loading of high heat polycarbonate could be reduced, and its impact strength and toughness could be transformed into a characteristics as valuable as, and existing simultaneously with, its resistance to thermal deformation, particularly when the high heat polycarbonate is blended with a polyester. A feature of this invention, therefore, is a blended composition of a high heat polycarbonate and a polyester which has a desirably high level of impact resistance and resistance to thermal deformation in combination with a desirably high level of chemical resistance and which is easily processed.

This invention involves a composition of matter containing, in admixture, (a) a high heat polycarbonate, (b) an aromatic polyester, and (c) a polyphenylene ether (including alloys thereof with styrenic polymers or copolymers), and (d) an elastomeric impact modifier.

This invention also involves a method of molding a high heat polycarbonate whereby high heat polycarbonate which has been admixed with an aromatic polyester, a polyphenylene ether and an elastomeric impact modifier is molded, in addition to a method of compounding or forming an article from a high heat polycarbonate composition. Further, this invention involves a method of strengthening, or reducing the notch sensitivity of, a high heat polycarbonate by blending it with an aromatic polyester, a polyphenylene ether and an elastomeric impact modifier. Blending a polycarbonate/polyester composition with a polyphenylene ether and an elastomeric impact modifier is also a method of providing an improved polycarbonate/polyester composition.

It has been found that a composition prepared by blending or admixing a high heat polycarbonate with an aromatic polyester, a polyphenylene ether, and an elastomeric impact modifier possesses Izod impact strength which is superior to that of high heat polycarbonate/polyester blends, and to that of such blends modified with only a polyphenylene ether or only an elastomeric impact modifier. It has also been found that the polycarbonate/polyester blended compositions of this invention have a unique balance of desirably high levels of resistance to solvents and thermal deformation and a desirably low level of notch sensitivity, and they are easily processed.

The compositions of this invention are useful, for example, in the production of films, fibers, extruded sheets, multi-layer laminates and molded or shaped articles of virtually all varieties, especially appliance and instrument housings, automobile body panels and other components for use in the automotive and electronics industries. The methods of this invention are useful for preparing compositions and molded articles having applications which are the same as or similar to the foregoing.

The compositions of this invention are those in which (a) a high heat polycarbonate has been admixed in a blended composition with (b) an aromatic polyester, and (c) a polyphenylene ether, and (d) an elastomeric impact modifier. Suitable ranges of content for components (a), (b), (c) and (d) in the compositions of this invention, expressed in parts by weight of the total composition, are as follows:

(a) polycarbonate from 30 parts to 93 parts, advantageously from 40 parts to 90 parts, preferably from 45 parts to 85 parts, more preferably from 50 parts to

80 parts, and most preferably from 55 parts to 75 parts,

(b) aromatic polyester from 5 parts to 69 parts, and preferably from 10 parts to 57 parts,

(c) polyphenylene ether from 1 part to 40 parts, advantageously from 1 part to 25 parts, preferably from 1 part to 15 parts, more preferably from 1 part to 10 parts, and most preferably from 1 part to 8 parts; and

(d) elastomeric impact modifier from 1 part to 25 parts, and preferably from 1 to 15 parts.

The compositions of this invention, and those formed by the methods of this invention, are typically characterized by a heat deflection temperature under load ("DTUL"), determined according to ASTM 648-82 at 66 psi, exceeding 270°F, advantageously exceeding 280°F, preferably exceeding 290°F, and more preferably exceeding 295°F.

Preparation of the compositions of this invention can be accomplished by any suitable mixing means known in the art. Typically the substances to be admixed with polycarbonate are dry blended in particulate form with sufficient agitation to obtain thorough distribution thereof within the polycarbonate. If desired, the dry-blended formulation can further, but need not, be melt mixed in an extruder, with or without a vacuum, or otherwise compounded with additional substances.

When softened or melted by the application of heat, the compositions of this invention can undergo fabrication and can therein be formed or molded using conventional techniques such as compression, injection molding, calendering, vacuum forming, extrusion and/or blow molding techniques, alone or in combination. The compositions can also be formed, spun or drawn into films, fibers, multi-layer laminates or extruded sheets, or can be compounded with one or more organic or inorganic substances, on any machine suitable for such purpose.

Compositions prepared within the ranges of content stated above possess Izod impact strength which is superior to that of high heat polycarbonate/polyester blends, and to that of such blends modified with only a polyphenylene ether or only an elastomeric impact modifier.

(a) Polycarbonate. A polycarbonate with good thermal stability - a high heat polycarbonate - is defined as that which has a glass transition temperature (T_g) in excess of 165°C, advantageously in excess of 175°C, preferably in excess of 185°C, and most preferably in excess of 195°C. T_g is the temperature or temperature range at which an amorphous polymeric material shows an abrupt change in its physical properties, including, for example, mechanical strength. T_g can be determined by differential scanning calorimetry.

The high heat polycarbonate suitable for use in this invention typically has a weight average molecular weight, as determined by gel permeation chromatography, of less than 40,000, advantageously less than 38,000, preferably less than 35,000, and more preferably less than 30,000. Because of its inherently high degree of resistance to thermal deformation, a polycarbonate which is characterized by high heat properties by reason of its structure, and which has in addition a weight average molecular weight exceeding 40,000, is difficult to heat soften for processing purposes. However, since a high heat polycarbonate having a lower molecular weight also has a higher ductile/brittle transition temperature, care must be taken that, in selecting a lower weight polycarbonate for easier processing, the result is not a composition formed therefrom which is brittle. One of the advantageous features of this invention, therefore, is a composition which has reduced notch sensitivity to impact loading and which, because of the presence of a high heat polycarbonate as described herein, has a desirably high level of heat resistance and is easily processed.

The polycarbonate involved in this invention can be prepared from those aromatic dihydroxy compounds which yield a high heat polycarbonate, being that which has a glass transition temperature (T_g) in excess of at least 165°C. The aromatic dihydroxy compounds which yield a high heat polycarbonate are typically derivatives of a diol such Bisphenol-A, and frequently are those which yield a polycarbonate product containing on the backbone of the repeating unit numerous bulky substituents, such as halogen, or higher or branched alkyl, aryl, alkoxy or aryloxy substituents or the like, and mixtures thereof.

Representative examples of high heat polycarbonates are those formed from dihydroxy compounds such as

(i) 2,2-bis(3,5-dihalo-4-hydroxyphenyl)propane ("Tetrahalo Bisphenol-A") where the halogen can be fluorine, chlorine, bromine or iodine, for example 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane ("Tetrabromo Bisphenol-A" or "TBBA");

(ii) 2,2-bis(3,5-dialkyl-4-hydroxyphenyl)propane ("Tetraalkyl Bisphenol-A") where the alkyl can be methyl or ethyl, for example 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane ("Tetramethyl Bisphenol-A");

(iii) 1,1-bis(4-hydroxyphenyl)-1-phenyl ethane ("Bisphenol-AP" or "Bis-AP");

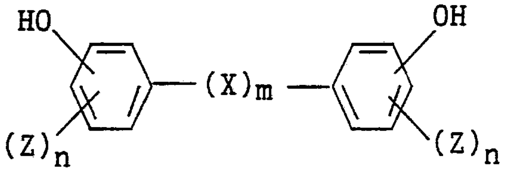
(iv) Bis(hydroxyphenyl)α-diphenylenemethane, ("Bis(hydroxyphenyl)fluorene");

or are copolymers formed from any of the foregoing dihydroxy compounds with other dihydroxy compounds, such as 2,2-bis(4-hydroxyphenyl)propane ("Bisphenol-A" or "Bis-A"). A polycarbonate formed from Bisphenol-A alone does not, however, meet the definition of a high heat polycarbonate of this invention.

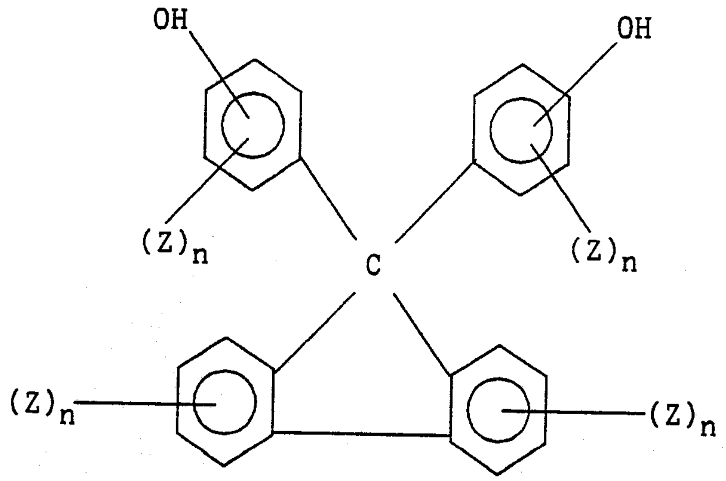
A dihydroxy compound capable of producing a high heat polycarbonate can be reacted with a carbonate precursor, such as a carbonic acid derivative. A carbonic acid derivative such as the carbonyl halide phosgene is useful for such purpose. A solution is formed of (i) an aromatic dihydroxy compound and a strong base in aqueous phase, and (ii) an inert, immiscible organic solvent which will dissolve both the carbonic acid derivative and the polycarbonate product. Solvents such as xylene or methylene chloride or other chlorinated hydrocarbons are suitable for such purpose. Caustic such as the the alkali or alkaline earth carbonates, oxides or hydroxides function best as the base, the total amount of which may be added at the beginning of, or incrementally during, the reaction. A pH of 10 to 13 is typically maintained throughout the reaction. The base forms the dianion of the aromatic dihydroxy compound in the aqueous phase, and the aqueous phase forms a continuous phase with the organic solvent dispersed, upon agitation, as droplets therein. Carbonic acid derivative is bubbled into this mixture, is dissolved in the organic solvent, and reacts with the aromatic dihydroxy compound at the interface of the droplets with the aqueous phase. Catalysts accelerate the rate of the reaction sufficiently to allow the formation of high molecular weight polycarbonates at the same low temperature at which the reaction began. Suitable catalysts for such purpose are tertiary amines such as triethylamine, N,N-dimethyl-cyclohexylamine or dimethyl-amino-pyridine, or quaternary ammonium bases such as tetramethyl ammonium hydroxide or triethyl benzyl ammonium hydroxide, or quaternary phosphonium, quaternary arsenium or tertiary sulfonium compounds. A bisaryl ester can be used in place of a carbonic acid derivative.

Polycarbonate can additionally be made by transesterification, which is accomplished by reacting a dihydroxy compound with a bis carbonic acid ester. A strongly alkaline catalyst such as the alkali metals and the alkaline earth metals and their oxides, hydrides or amides, or the basic metal oxides such as zinc oxide, lead oxide and antimony oxide is used as an accelerator, and the reaction is run at temperatures of between 150°C and 300°C, using vacuum to remove the residue of the bis carbonic acid ester. At temperatures between 150°C and 200°C, low molecular weight polycarbonate terminated with bis carbonic acid ester groups is formed, which can then interreact at temperatures above 250°C to form higher weight polycarbonate by splitting off the original bis carbonic acid ester. This process is carried out at reduced pressure.

Suitable dihydroxy compounds for the preparation of high heat polycarbonate are those wherein the sole reactive groups are two hydroxyl groups, such as variously bridged, substituted or unsubstituted aromatic diols ("bisphenols"), or mixtures thereof, represented by the general formula



where (i) X is a substituted or unsubstituted, linear or cyclic, divalent hydrocarbon radical containing 1-20 carbon atoms, or is a mixture of more than one of such radicals, or is -S-, -S-S-, -SO-, SO_2-, -O-, -CO-, or a single bond; (ii) Z is independently hydrogen; a halogen such as fluorine, chlorine, bromine or iodine; or is a monovalent organic radical such as an alkyl group of 1-4 carbons, an aryl group of 6-8 carbons (*e.g.* phenyl, tolyl, xylyl or the like), an alkoxy group of 1-4 carbons, or an aryloxy group of 6-8 carbons, provided that at least one Z is not hydrogen; and (<u>iii</u>) m is 0 or 1, and n is 1-4 inclusive. For example, Bis(hydroxyphenyl)fluorene can be represented by the formula



where Z and n are as set forth above except that each Z may be hydrogen.

When the high heat character of a polycarbonate, as indicated by a T_g or DTUL in the ranges set forth above, derives from the presence of halogen substituents (such as chlorine or bromine) on a dihydroxy compound, the high heat polycarbonate will typically contain at least 20 percent halogen by weight.

The carbonate polymers employed in the present invention can also be high heat polycarbonates based on dihydroxy benzenes such as pyrocatechol, resorcinol and hydroquinone (and their halo- and alkyl-substituted derivatives), and on dihydroxy naphthalenes and anthracenes.

Although the polycarbonates mentioned above, such as those derived from Bis(hydroxyphenyl) fluorene or from Bisphenol-AP, can each be employed in this invention as a homopolymer (*i.e.* the product obtained when only one dihydroxy compound is used to prepare the polycarbonate), the carbonate polymers used herein can also be derived from two or more different dihydroxy compounds, or mixtures thereof, in the event a carbonate copolymer or interpolymer rather than a homopolymer is desired. For example, a typical copolymer is that which is made from Bisphenol-A and Tetrabromo Bisphenol-A wherein the Tetrabromo Bisphenol-A is present in at least the amount of twenty percent by weight.

Copolymers can also be formed when a bisphenol is reacted with a carbonic acid derivative and a polydiorganosiloxane containing α,ω-bishydroxyaryloxy terminal groups to yield a siloxane/carbonate block copolymer (as are discussed in greater detail in Paul, USP 4,569,970), or when a bisphenol is reacted with a dicarboxylic acid (or ester-forming derivative) or with a bis(ar-haloformylaryl) carbonate to yield an alternating copolyestercarbonate, the bis(ar-haloformylaryl) carbonate being formed by reacting a hydroxycarboxylic acid with a carbonic acid derivative under carbonate forming conditions. Copolyestercarbonates are discussed in greater detail in Swart, USP 4,105,533.

Also useful in this invention are physical blends of two or more of the carbonate homo- and/or copolymers described above. The term "polycarbonate" as used herein, and in the claims appended hereto, should therefore be understood to include carbonate homopolymers, carbonate copolymers (as described above), and/or blends of various carbonate homopolymers and/or various carbonate copolymers, so long as the resulting homopolymer or copolymer has a T_g exceeding at least 165°C. Where a blend of more than one carbonate homopolymer and/or copolymer is used, the blend of such polycarbonates, if miscible, will have a T_g exceeding at least 165°C. In the case where a blend of high heat polycarbonates is immiscible, the component(s) constituting more than 50 weight percent of such blend of polycarbonates will have a T_g exceeding at least 165°C.

The methods generally described above for preparing carbonate polymers suitable for use in the practice of this invention are known; for example, several methods are discussed in detail in Schnell, USP 3,028,365; Campbell, USP 4,384,108; Glass, USP 4,529,791; and Grigo, USP 4,677,162.

(b) Polyester. The aromatic polyester used in this invention may be made by the self-esterification of hydroxycarboxylic acids, or direct esterification, which

involves the reaction of a diol with a dicarboxylic acid with the resulting elimination of water, giving an -[-AABB-]- polyester. Temperatures applied exceed the melting points of the reactants and typically approach the boiling point of the diol being used, and usually range from 150°C to 280°C. An excess of the diol is typically used, and once all of the acid has reacted with diol, the excess diol is removed by distillation with the application of additional heat under reduced pressure.

Alternatively, but in like manner, ester-forming derivatives of a dicarboxylic acid can be heated with a diol to obtain polyesters in an ester interchange reaction. Suitable acid derivatives for such purpose are esters, halides, salts or anhydrides of the acid. The ester interchange reaction is typically run in the presence of a diluent, for example, an inert organic solvent such as chloroform or tetrachloroethane, and in the presence of a base, for example a tertiary organic base such as pyridine. Typical catalysts used when ester interchange involves alcoholysis are weak bases such as carbonates or alkoxides of sodium, lithium, zinc, calcium, magnesium or aluminum, whereas catalysts such as antimony oxide, titanium butoxide or sodium acetate are often used when acidolysis occurs in the interchange reaction. Diol derivatives such as an acetate can be used effectively when it is desired to conduct acidolysis.

The molecular weight of polyester can be increased by adding a chain coupling agent, such as diphenyl carbonate, to the melt reaction mixture just prior its completion. Or, to achieve higher weight by solid state polymerization, polyester product of intermediate weight can be heated in a vacuum or stream of inert gas, first to a temperature where it crystallizes and then to a temperature close to its melting point.

Polyesters can also be produced by a ring-opening reaction of cyclic esters or lactones, for which organic tertiary bases and alkali and alkaline earth metals, hydrides and alkoxides can be used as initiators.

Suitable reactants for making the polyester used in this invention, in addition to hydroxycarboxylic acids, are diols and dicarboxylic acids either or both of which can be aliphatic or aromatic. A polyester which is a poly(alkylene alkanedicarboxylate), a poly(alkylene phenylenedicarboxylate), a poly(phenylene alkanedicarboxylate), or a poly(phenylene phenylenedicarboxylate) is therefore appropriate for use herein. Alkyl portions of the polymer chain can be substituted with, for example, halogens, alkoxy groups or alkyl side chains and can contain divalent heteroatomic groups (such as -O-, -S- or $-SO_2-$) in the paraffinic segment of the chain. The chain can also contain unsaturation and non-aromatic rings. Aromatic rings can contain substituents such as halogens, alkoxy or alkyl groups, and can be joined to the polymer backbone in any ring position and directly to the alcohol or acid functionality or to intervening atoms.

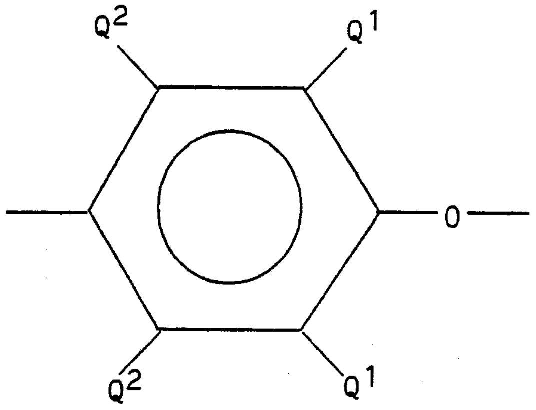
Typical alkylene diols used in ester formation are the C_2-C_{10} glycols, such as ethylene-, propylene-, and butylene glycol. Alkanedicarboxylic acids frequently used are oxalic acid, adipic acid and sebacic acid. Diols which contain rings can be, for example, a 1,4-cyclohexylenyl glycol or a 1,4-cyclohexanedimethylene glycol, resorcinol, hydroquinone, 4,4'-thiodiphenol, bis-(4-hydroxyphenyl)sulfone, a dihydroxynaphthalene, a xylylene diol, or can be one of the many bisphenols such as 2,2-bis-(4-hydroxyphenyl) propane. Aromatic diacids include, for example, terephthalic acid, isophthalic acid, naphthalenedicarboxylic acid, diphenyletherdicarboxylic acid, diphenyldicarboxylic acid, diphenylsulfonedicarboxylic acid, diphenoxyethanedicarboxylic acid.

In addition to polyesters formed from one diol and one diacid only, the term "polyester" as used herein includes random, patterned or block copolyesters, for example those formed from two or more different diols and/or two or more different diacids, and/or from other divalent heteroatomic groups. Mixtures of such copolyesters, mixtures of polyesters derived from one diol and diacid only, and mixtures of members from both of such groups, are also all suitable for use in this invention, and are all included in the term "polyester". For example, use of cyclohexanedimethylol together with ethylene glycol in esterification with terephthalic acid forms a clear, amorphous copolyester ("PETG") of particular interest. Also contemplated are PCTG; liquid crystalline polyesters derived from mixtures of 4-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid; or mixtures of terephthalic acid, 4-hydroxybenzoic acid and ethylene glycol; or mixtures of terephthalic acid, 4-hydroxybenzoic acid and 4,4'-dihydroxybiphenyl.

Aromatic polyesters, those prepared from an aromatic diacid, such as the poly(alkylene phenylenedicarboxylates) polyethylene terephthalate and polybutylene terephthalate, or mixtures thereof, are particularly useful in this invention.

Methods and materials useful for the production of polyesters, as described above, are discussed in greater detail in Whinfield, US Pat. No. 2,465,319, Pengilly, US Pat. No. 3,047,539 and Russell, US Pat. No. 3,756,986.

(c) Polyphenylene ether. The polyphenylene ethers (also known as polyphenylene oxides) useful in this invention comprise a plurality of structural units described generally by the formula



In each of said units independently, each Q^1 is independently halogen, primary or secondary lower alkyl (*i.e.*, alkyl containing up to 7 carbon atoms), phenyl, haloalkyl, aminoalkyl, hydrocarbonoxy, or halohydrocarbonoxy wherein at least two carbon atoms separate the halogen and oxygen atoms; and each Q^2 is independently hydrogen, halogen, primary or secondary lower alkyl, phenyl, haloalkyl, hydrocarbonoxy or halohydrocarbonoxy as defined for Q^1. Examples of suitable primary lower alkyl groups are methyl, ethyl, n-propyl, n-butyl, isobutyl, n-amyl, isoamyl, 2-methylbutyl, n-hexyl, 2,3-dimethylbutyl, 2-, 3- or 4-methylpentyl and the corresponding heptyl groups. Examples of secondary lower alkyl groups are isopropyl, sec-butyl and 3-pentyl. It is preferred that any alkyl radicals are straight chain rather than branched. Most often, each Q^1 is alkyl or phenyl, especially C_{1-4} alkyl, and each Q^2 is hydrogen.

Both homopolymer and copolymer polyphenylene ethers are included. Suitable homopolymers are those containing, for example, 2,6-dimethyl-1,4-phenylene ether units. Suitable copolymers include random copolymers containing such units in combination with, for example, 2,3,6-trimethyl-1,4-phenylene ether units.

Also included are polyphenylene ethers containing moieties which modify properties such as molecular weight, melt viscosity and/or impact strength. Such polymers may be prepared by grafting onto the polyphenylene ether, in known manner, such vinyl monomers as acrylonitrile and vinylaromatic compounds (*e.g.,* styrene), or such polymers as polystyrenes and elastomers. The product typically contains both grafted and ungrafted moieties. Other suitable polymers are the coupled polyphenylene ethers in which the coupling agent is reacted, in known manner, with the hydroxy groups of two polyphenylene ether chains to produce a higher molecular weight polymer containing the reaction product of the hydroxy groups and the coupling agent.

Illustrative coupling agents are low molecular weight polycarbonates, quinones, heterocycles and formals.

The polyphenylene ether generally has a number average molecular weight within the range of 3,000-40,000, and a weight average molecular weight within the range of 20,000-80,000, as determined by gel permeation chromatography. Its intrinsic viscosity is most often in the range of 0.15-0.6, and preferably at least 0.25, dL/g, as measured in chloroform at 25°C.

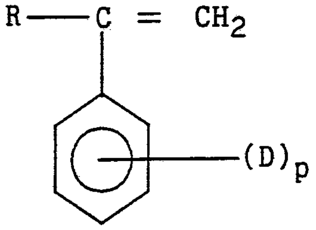
The polyphenylene ethers are typically prepared by the oxidative coupling of at least one corresponding monohydroxyaromatic compound. Particularly useful and readily available monohydroxyaromatic compounds are 2,6-xylenol (wherein each Q^1 is methyl and each Q^2 is hydrogen), whereupon the polymer may be characterized as a poly(2,6-dimethyl-1,4-phenylene ether), and 2,3,6-trimethylphenol (wherein each Q^1 and one Q^2 is methyl and the other Q^2 is hydrogen).

A variety of catalyst systems are known for the preparation of polyphenylene ethers by oxidative coupling. For the most part, such catalysts contain at least one heavy metal compound such as a copper, manganese or cobalt compound, usually in combination with various other materials.

A first class of preferred catalyst systems consists of those containing a copper compound, such as are disclosed, for example, in U.S. Pat. Nos. 3,306,874, 3,306,875, 3,914,266 and 4,028,341, which are incorporated herein. They are usually combinations of cuprous or cupric ions, halide (*i.e.*, chloride, bromide or iodide) ions and at least one amine.

Catalyst systems containing manganese compounds constitute a second preferred class. They are generally alkaline systems in which divalent manganese is combined with such anions as halide, alkoxide or phenoxide. Most often, the manganese is present as a complex with one or more complexing and/or chelating agents such as dialkylamines, alkanolamines, alkylenediamines, *o*-hydroxyaromatic aldehydes, *o*-hydroxyazo compounds, ω-hydroxyoximes (monomeric and polymeric), *o*-hydroxyaryl oximes and β-diketones. Also useful are known cobalt-containing catalyst systems.

The polyphenylene ether used herein may also be blended with at least one polystyrene. The term "polystyrene" includes polymers prepared by bulk, suspension or emulsion polymerization which contain at least 25 percent by weight structural units derived from a monomer described generally by the formula



wherein R is hydrogen, C_{1-8} lower alkyl or halogen, D is C_{1-8} vinyl, halogen or C_{1-8} lower alkyl, and p is from 0 to 5. These resins include homopolymers of styrene, chlorostyrene and vinyltoluene; random copolymers of styrene with one or more monomers illustrated by acrylonitrile, an alkyl acrylate, butadiene, α-methylstyrene, ethylvinylbenzene, divinylbenzene, maleic anhydride and phenyl maleimide; an ethylene/propylene/diene copolymer grafted with acrylonitrile and styrene; and rubber modified polystyrenes comprising blends and grafts, wherein the rubber is a polybutadiene or a rubbery copolymer of 70-98 percent styrene and 2-30 percent diene monomer. The polystyrenes may also be rubber modified by blending with a hydrogenated or unhydrogenated styrene/butadiene block copolymer, containing at least fifty percent styrene by weight, to create a high impact polystyrene ("HIPS").

The proportion of such polystyrene in the polyphenylene ether of this invention is not critical, since polyphenylene ether and styrenic polymers and copolymers are miscible in all proportions, but will typically be 5-50 percent by weight, if any.

Polyphenylene ethers, as described above, are discussed in greater detail in U.S. Pat. No. 4,866,130, which is incorporated herein in its entirety.

(d) Elastomeric Impact Modifier. The elatomeric impact modifier used in this invention is a rubbery or elastomeric substance, typically with a T_g less than 10°C, and preferably less than -5°C, which is suitable or effective for the purpose of imparting enough flexibility and freedom of chain rotation to a polycarbonate/polyester blend to improve its toughness; reduce its notch sensitivity; and enable it, in response

to the deformation of an applied stress, to recover with stored modulus rather than fracture. The rubber content of the impact modifier used in this invention is typically greater than 40 percent by weight, and a mixture of two or more elastomeric substances can be used as the impact modifier.

Illustrative examples of elastomeric impact modifiers useful in this invention are thermoplastic elastomers, emulsion-type, core-shell graft copolymer elastomers, and olefinic elastomers.

The thermoplastic elastomers useful in this invention are characterized, for example, in that they can be melted and recooled, or dissolved and reformed upon removal of the solvent, without undergoing any significant change in properties. Thermoplastic elastomers are also characterized by the randomness of the shape and size they take on when mixed by shearing forces with the other components making up the compositions of this invention, especially when heat is applied during such mixing. Because the thermoplastic elastomer is typically a long chain molecule, segments of thermoplastic elastomer in the polymer composition matrix are generally elongated, linear ribbons or bands. The molecules tend to fuse and flow together in a continuous structure. However, chain coiling can yield globule-shaped segments of thermoplastic elastomer in the matrix.

The random shape and size assumed in the polymer composition matrix by a thermoplastic elastomer is to be distinguished from the shape and size assumed by a core-shell graft copolymer. A core-shell graft copolymer is typically present in the polymer matrix in a bead shape both before and after mixing by application of shearing forces, whether heat is used or not, and is usually present in a rather narrow size range, for example 0.05-0.8 microns. The retention of this core-shell, or spherical, shape by the graft polymer, even after heating and mixing, results from the fact that the outer layers, which surround the core, are formed by grafting appropriate monomers onto the core. A core-shell graft copolymer typically cannot be melted and recooled without a significant change in properties because the graft polymer will tend to decompose or crosslink, and the bead-shaped segments of graft polymer will tend to agglomerate upon melting, making dispersion of them by mixing difficult.

(d)(i). Thermoplastic elastomers include, for example, block copolymers which can be either linear or branched, and can be either a di-block ("A-B") copolymer, tri-block ("A-B-A") copolymer, or radial teleblock copolymer with or without tapered sections, *i.e.* portions of the polymer where the monomers alternate or are in random order close to the point of transition between the A and B blocks. The A portion is made by polymerizing one or more mono-alkenyl or vinyl aromatic hydrocarbon monomers, and has an average molecular weight of 4,000 to 115,000, and a weight preferably of 8,000 to 60,000. The B portion of the block copolymer results from polymerizing a diene and has a molecular weight of 20,000 to 450,000, and a weight preferably of 50,000 to 300,000. In the A-B di-block copolymer, each block, A or B, can vary from 10-90 weight percent of the total weight of the copolymer. In the A-B-A tri-block copolymer, the A end groups typically constitute 2

weight percent to 55 weight percent of the whole block copolymer, and preferably are between 5 weight percent and 30 weight percent of the whole block copolymer.

The A block of the block copolymer has properties characteristic of thermoplastic substances in that it has the stability necessary for processing at elevated temperatures and yet possesses good strength below the temperature at which it softens. The A block is polymerized predominantly from vinyl aromatic hydrocarbons, and substituted derivatives thereof wherein the aromatic moiety can be either mono- or polycyclic. Monomers from which the thermoplastic end blocks can be formed are, for example, styrene and substituted derivatives thereof such as α-methyl styrene, vinyl xylene, vinyl naphthalene, and the like, and mixtures of two or more thereof. Other vinyl monomers such as methyl acrylate, methyl methacrylate, acrylonitrile or vinyl pyridine may be used in the formation of the A block together with the aromatic monomers. The polymerization can be initiated by lithium metal, or alkyl- or aryl lithium compounds such as butyl lithium or isoamyl lithium. Polymerization is normally conducted at temperatures ranging from -20°C to 100°C.

The B block of the copolymer can be formed, for example, simply by injecting suitable monomer into the reaction vessel and displacing the lithium radical from the just-polymerized A block, which then acts as an initiator because it is still charged. The B block is formed predominantly from substituted or unsubstituted C_2-C_{10} dienes, particularly conjugated dienes such as butadiene or isoprene. Other diene, vinyl or olefinic monomers such as chloroprene, 1,4-pentadiene, isobutylene, ethylene or vinyl chloride may be used in the formation of the B block provided that they are present at a level low enough to not alter the fundamental olefinic character of the B block. The mid block will be characterized by elastomeric properties which allow it to to absorb and dissipate an applied stress and then regain its shape.

In the A-B-A tri-block copolymer, the second end block A can be formed in a manner similar to the first, by injecting appropriate alkenyl aromatic monomer (as described above) into the reaction vessel.

To reduce oxidative and thermal instability, the block copolymers used herein can also desirably be hydrogenated to reduce the degree of unsaturation on the polymer chain and on the pendant aromatic rings. The block copolymer may be selectively hydrogenated by hydrogenating only the elastomeric block B. Typical hydrogenation catalysts utilized are Raney nickel, molybdenum sulfide, finely divided palladium and platinum oxide. The hydrogenation reaction is typically run at 75-450°F and at 100-1,000 psig for 10-25 hours.

The most preferred block thermoplastic elastomers are vinyl aromatic/conjugated diene block copolymers formed from styrene and butadiene or styrene and isoprene. When the styrene/butadiene copolymers are hydrogenated, they are frequently represented as styrene/ethylene/butylene (or styrene/ethylene/butylene/styrene in the tri-block form) copolymers. When the styrene/isoprene copolymers are hydrogenated, they are frequently represented as styrene/ethylene/propylene (or styrene/ethylene/propylene/styrene in the tri-block form) copolymers. The block copolymers described above are discussed in greater detail in Holden, USP 3,265,766; Haefele, USP 3,333,024; Wald, USP 3,595,942; and Witsiepe, USP 3,651,014.

Thermoplastic elastomers also include A-B-A or A-B block copolymers which have a rigid block "A" having a T_g above room temperature (approximately 23-25°C) and a rubbery block "B" having a T_g below room temperature prepared from substances other than those described above. Examples of typical pairings of other materials to form the respective A and B blocks of a block copolymer thermoplastic elastomer are shown in Table I.

Table I
Block Copolymer Pairings

A block	B block
polyethylene	ethylene/butylene copolymer
polyurethane	polyester polyether
polyester	polyether
polypropylene	EPDM rubber

Block copolymer thermoplastic elastomers can be prepared, for example, by anionic polymerization using an alkyl-lithium initiator. Thermoplastic elastomers based on urethane are discussed in greater detail in Schollenberger, USP 3,015,650 and Saunders, USP

3,214,411; and those based on copolyester-ether are discussed in Witsiepe, USP 3,651,014.

(d)(ii). The core-shell graft copolymer elastomers used in this invention can be based on either a diene rubber, an acrylate rubber or on mixtures thereof.

A diene rubber contains a substrate latex, or core, which is made by polymerizing a diene, preferably a conjugated diene, or by copolymerizing a diene with a mono-olefin or polar vinyl compound, such as styrene, acrylonitrile, or an alkyl ester of an unsaturated carboxylic acid such as methyl methacrylate. The substrate latex is typically made up of 40-85 percent diene, preferably a conjugated diene, and 15-60 percent of the mono-olefin or polar vinyl compound. The elastomeric core phase should have a glass transition temperature ("T_g") of less than 10°C, and preferably less than -20°C. A mixture of monomers is then graft polymerized to the substrate latex. A variety of monomers may be used for this grafting purpose, of which the following are exemplary: vinyl compounds such as vinyl toluene or vinyl chloride; vinyl aromatics such as styrene, alpha-methyl styrene or halogenated styrene; acrylonitrile, methacrylonitrile or alpha-halogenated acrylonitrile; a C_1-C_8 alkyl acrylate such as ethyl acrylate or hexyl acrylate; a C_1-C_8 alkyl methacrylate such as methyl methacrylate or hexyl methacrylate; acrylic or methacrylic acid; and the like or a mixture of two or more thereof.

The grafting monomers may be added to the reaction mixture simultaneously or in sequence, and, when added in sequence, layers, shells or wart-like appendages can be built up around the substrate latex, or core. The monomers can be added in various ratios to each other although, when just two are used, they are frequently utilized in equal amounts. A typical weight ratio for methyl methacrylate/butadiene/styrene copolymer ("MBS" rubber) is 60-80 parts by weight substrate latex, 10-20 parts by weight of each of the first and second monomer shells. A preferred formulation for an MBS rubber is one having a core built up from 71 parts of butadiene, 3 parts of styrene, 4 parts of methyl methacrylate and 1 part of divinyl benzene; a second phase of 11 parts of styrene; and a shell phase of 11 parts of methyl methacrylate and 0.1 part of 1,3-butylene glycol dimethacrylate, where the parts are by weight of the total composition. A diene-based, core-shell graft copolymer elastomer and methods for making same, as described above, are discussed in greater detail in Saito, USP 3,287,443, Curfman, USP 3,657,391, and Fromuth, USP 4,180,494.

An acrylate rubber has a first phase forming an elastomeric core and a second phase forming a rigid thermoplastic phase said elastomeric core. The elastomeric core is formed by emulsion or suspension polymerization of monomers which consist of at least 50 weight percent alkyl and/or aralkyl acrylates having up to fifteen carbon atoms, and, although longer chains may be used, the alkyls are preferably C_2-C_6, most preferably butyl acrylate. The elastomeric core phase should have a T_g of less than 10°C, and preferably less than -20°C.

The rigid thermoplastic phase of the acrylate rubber is formed on the surface of the elastomeric core using suspension or emulsion polymerization techniques. The monomers necessary to create this phase together with necessary initiators are added directly to the reaction mixture in which the elastomeric core is formed, and polymerization proceeds until the supply of monomers is substantially exhausted. Monomers such as an alkyl ester of an unsaturated carboxylic acid, for example a C_1-C_8 alkyl acrylate like methyl acrylate, hydroxy ethyl acrylate or hexyl acrylate, or a C_1-C_8 alkyl methacrylate such as methyl methacrylate or hexyl methacrylate, or mixtures of any of the foregoing, are some of the monomers which can be used for this purpose. Either thermal or redox initiator systems can be used. Because of the presence of the graft linking agents on the surface of the elastomeric core, a portion of the chains which make up the rigid thermoplastic phase are chemically bonded to the elastomeric core. It is preferred that there be at least 20 percent bonding of the rigid thermoplastic phase to the elastomeric core.

A preferred acrylate rubber is made up of more than 40 percent to 95 percent by weight of an elastomeric core and 60 percent to 5 percent of a rigid thermoplastic phase. The elastomeric core can be polymerized from 75 percent to 99.8 percent by weight C_1-C_6 acrylate, preferably n-butyl acrylate. The rigid thermoplastic phase can be polymerized from at least 50 percent by weight of C_1-C_8 alkyl methacrylate, preferably methyl methacrylate. Acrylate rubbers and methods for making same, as described above, are discussed in greater detail in Owens, USP 3,808,180 and Witman, USP 4,299,928.

(d)(iii). Olefinic elastomers useful as an impact modifier in this invention are based generally on a long-chain, hydrocarbon backbone, which may or may not be grafted with one or more vinyl monomers. Representative examples of a few olefinic elastomers which illustrate the variation in the known substances which would suffice for such purpose are as follows: butyl rubber, chlorosulfonated polyethylene rubber, ethylene/propylene copolymer, ethylene/propylene/diene copolymer, fluorinated olefins, neoprene rubber, nitrile rubber, polybutadiene and polyisoprene.

The olefinic elastomer used herein may also contain reactive moieties. A reactive olefinic elastomer may, for example, be a polymer which has a glass transition temperature (T_g) less than 0°C formed from (A) (I) at least one olefin monomer such as ethylene, propylene, isopropylene, butylene or isobutylene, or at least one conjugated diene such as butadiene, and the like, or mixtures thereof, or (II) a copolymer of one or more olefin monomers, such as described above, with other vinyl monomer(s), but containing a sufficient amount of the olefin monomer(s) to impart a T_g of less than 0°C to the reactive olefinic elastomer; (B) at least one vinyl (*i.e.* olefinically unsaturated, including vinylidene) or olefin monomer carrying at least one epoxide group; and, optionally, (C) at least one vinyl (*i.e.* olefinically unsaturated, including vinylidene) monomer not carrying an epoxide group.

Representative vinyl (*i.e.* olefinically unsaturated, including vinylidene) monomers useful as the optional component (C) in forming the polymeric reactive olefinic elastomer of this invention include the following: vinyl compounds (especially when they bear a polar, electronegative group or functionality) such as vinyl toluene, alphamethyl styrene, halogenated styrene; those containing nitrile groups such as copolymers of acrylonitrile, methacrylonitrile or alpha-halogenated acrylonitrile; a C_1-C_8 alkyl acrylate such as ethyl acrylate, butyl acrylate, hexyl acrylate or hydroxy ethyl acrylate; a C_1-C_8 alkyl methacrylate such as methyl methacrylate or hexyl methacrylate; an acrylic or methacrylic acid; the vinylidene monomers, especially when they bear a polar, electronegative group or functionality such as a halogen group, or an organic group having a double or triple bond such as phenyl, carboxy, cyano or the like; vinyl esters or vinyl ethers; alkenyl-aromatic compounds such as styrene and substituted derivatives thereof; maleimides; mononitriles having alpha-beta-olefinic unsaturation and lower alkyl or halogen substituents; aliphatic vinyl compounds such as vinyl chloride, vinylidene chloride, acrylic and methacrylic acid esters, amides and nitriles, vinyl acetate, vinyl propionate and vinyl benzoate; vinyl-methyl-ether, vinyl-ethyl-ether and vinyl-isobutyl-ether; and aromatic vinyl compounds such as styrene, alpha -methyl styrene, vinyl toluene, p-ethylstyrene, 2,4-dimethyl styrene, o-chlorostyrene and 2,5-dichlorostyrene; vinyl esters; vinyl ethers; alpha-olefins; vinyl toluenes; vinyl xylenes; the maleates; the fumarates; and the like; or mixtures of two or more of any of the foregoing. In general, vinyl and vinylidene monomers from groups such as the vinyl and vinylidene -esters, -ethers, -organic acids, -aromatics, -alcohols, -anhydrides, -halides, -nitriles and -amides; or mixtures of any of the foregoing may be used.

Additionally, any one or more of the foregoing monomers may be copolymerized with carbon monoxide.

Vinyl monomers such as the foregoing may also be copolymerized as part of the olefin copolymer described above as component (A)(II); or, when carrying an epoxide group, may be used as the component (B). Or, the epoxide group may be carried on an olefin monomer.

Suitable olefinically unsaturated monomers containing epoxide groups for use as component (B) of the terpolymeric reactive olefinic elastomer include, for example, glycidyl esters of unsaturated carboxylic acids (glycidyl methacrylate); glycidyl ethers of unsaturated alcohols (allyl-glycidyl-ether) and of alkenylphenols (isopropenylphenyl-glycidylether); and vinyl and allyl esters of epoxycarboxylic acids (vinyl esters of epoxidized oleic acid). In general, all compounds which contain both a polymerizable unsaturated group and reactive epoxide groups in the molecule can be used for preparation of the reactive olefinic elastomer of the invention.

Copolymers of 1-25 percent (by weight) of glycidyl methacrylate, 40-95 percent of ethylene, and 4-40 percent of vinyl acetate are particularly suitable for use herein as the polymeric reactive olefinic elastomer. When the optional component (C) is not present in the reactive olefinic elastomer, a copolymer of 1-25 percent (by weight) of glycidyl methacrylate, 75-99 percent of ethylene is preferred.

Copolymers containing epoxide groups may be obtained according to known processes, for example by radical polymerization in chlorobenzene at 80°C in 50 percent strength solution. For instance, monomers such as listed above are dissolved in an appropriate solvent, such as benzene, chlorobenzene or toluene, and polymerized at a temperature of 80°C by adding azobisisobutyronitrile, whereby oxygen is excluded. After the monomers have been reacted, the solvent used is distilled off (*e.g.*, chlorobenzene at 100°C and 20 torr) and the residue is dried in vacuum at 100°C and then powdered. The terpolymeric reactive olefinic elastomer of this invention can also be prepared in gas phase under conditions suitable for polymerizing an olefin. For example, the terpolymer can be made in either a tubular reactor or a stirred autoclave, where heated, pressurized feed streams of olefin or vinyl monomer gas, peroxide free-radical initiator and chain transfer agent are injected into the reaction device. The reaction of formation usually occurs at 1,500-3,000 atm (152-304 MPa) and at a temperature usually not exceeding 300°C, as known in the art.

The molecular weight of the reactive olefinic elastomer is typically between 10,000 and 500,000, preferably between 30,000 and 200,000, and it typically contains 5 to 1,000, preferably 20 to 500, epoxide groups per macromolecule.

A variety of other additives may be used in the compositions of this invention for protection against thermal, oxidative and ultra-violet degradation. Representative of the thermal and oxidative stabilizers which can advantageously be utilized herein are hindered phenols, hydroquinones, phosphites, including substituted members of those groups and/or mixtures of more than one thereof. A preferred phenolic anti-oxidant is Irganox™ 1076 anti-oxidant, available from Ciba-Geigy Corp. Ultra-violet stabilizers such as various substituted resorcinols, salicylates, benzotriazoles, benzophines, hindered amines and hindered phenols can also be usefully included in the compositions of this invention, as can be lubricants, colorants, fillers such as talc, clay, phosphate, metal, inorganic or graphite fibers, or mica, pigments, ignition resistant additives and mold release agents, and reinforcement agents such as fiberglass or phosphate, metal, inorganic or graphite fibers. Use and selection of the aforenamed additives and stabilizers, and others of like kind, may be made by one skilled in the art. Such additives, if used, typically do not exceed 5 percent by weight of the total composition, except fillers or reinforcing agents, which may constitute up to 40 percent of the composition.

Illustrative Embodiments. To illustrate the practice of this invention, examples of several preferred embodiments are set forth below. It is not intended, however, that these examples (Examples 1-24) should in any manner restrict the scope of this invention. Some of the particularly desirable features of this invention may be seen by contrasting the characteristics of Examples 1-24 with those of controlled formulations (Control A-K) which do not possess the features of, and are not therefore embodiments of, this invention.

The polycarbonate compositions prepared in Controls A-K and Examples 1-24 were made by dry blending the ingredients thereof and agitating same in a paint shaker for 7 minutes. The dry blended formulations were then melt mixed in a vented 30mm Werner-Pfleiderer co-rotating, twin screw extruder using a 250 rpm speed and a set temperature in the range of 290°C-320°C, the set temperature being sufficient in relation to the T_g of the material to obtain melting thereof in the extruder. Each extruded composition was passed through a water bath, chopped into granules and collected for molding. Granules were thoroughly dried in a circulated air oven at 115°C for six hours prior to molding. All samples were prepared by injection molding on a 75 ton (6.8×10^4 kg) Arburg molding machine. Molding temperatures for the barrel and mold were set at 290°C-310°C and 190°C, respectively.

The formulations of the polycarbonate compositions of Controls A-H are given below in Table II in parts by weight of the total composition. In Table II:

"(1) Bisphenol-AP PC" is a polycarbonate prepared from Bisphenol-AP [1,1-bis(4-hydroxyphenyl)-1-phenyl ethane] having a T_g of 190°C and a weight average molecular weight of 30,000;

"(2) Brominated PC I" is a polycarbonate prepared from mixture of Bisphenol-A ("Bis-A") and Tetrabromo Bisphenol-A ("TBBA") in a 2/1 Bis-A/TBBA molar ratio, having a T_g of 190°C and a weight average molecular weight of 30,000;

"(3) Brominated PC II" is a polycarbonate prepared from mixture of Bisphenol-A ("Bis-A") and Tetrabromo Bisphenol-A ("TBBA") in a 4/1 Bis-A/TBBA molar ratio, having a T_g of 175°C and a weight average molecular weight of 30,000;

"(4) Polyester" is a polyethylene terephthalate having an inherent viscosity of 1.04 (determined according to ASTM Designation D 4603-86), available as 1006 polyester from Goodyear Tire and Rubber Co.;

"(5) Polyphenylene Ether I" is Noryl™ N300 polyphenylene ether/styrenic polymer alloy, having a deflection temperature under load of 300°F (determined according to ASTM Designation D648-82), available from General Electric Company;

"(6) Kraton™G 1651" is a hydrogenated styrene/butadiene block thermoplastic elastomer copolymer from Shell Oil Company;

"(7) E/VA/GMA" is a terpolymer containing ethylene, vinyl acetate and glycidyl methacrylate and having a weight-average molecular weight of approximately 100,000, available from Sumitomo Chemical America; and

"(8) GRC 120" is a core-shell graft polymer containing approximately 50 percent rubber wherein styrene and acrylonitrile are grafted onto a butadiene core.

Table II

Content of Controls A-H in parts by weight

	A	B	C	D	E	F	G	H
(1) Bisphenol-AP PC	1,300	1,300	1,300	1,200	800	--	--	1,300
(2) Brominated PC I	--	--	--	--	--	1,300	--	--
(3) Brominated PC II	--	--	--	--	--	--	1,300	--
(4) Polyester	500	500	500	500	750	500	500	500
(5) Polyphenylene Ether I	--	--	--	--	--	--	--	200
(6) Kraton™ G 1651	200	--	--	100	200	--	200	--
(7) E/VA/GMA	--	200	--	200	250	200	--	--
(8) GRC 120	--	--	200	--	--	--	--	--

The results of several tests performed on the blended polycarbonate compositions of Controls A-H are shown below in Table III. In Table III:

"(1) DTUL" is deflection temperature under load as measured in accordance with ASTM Designation D 648-82 at 66 psi;

"(2) Izod" is impact resistance as measured by the Izod test according to ASTM Designation D 256-84 (Method A) at 23°C. The notch was 10 mils (0.254 mm) in radius, and was cut so that the flexural shock caused by the striking nose of the pendulum was propagated parallel to the direction of flow taken by the molten extrudate during formation of the sample;

"(3) Weldline" is also measured by the Izod test according to ASTM Designation D 256-84 (Method A) at 23°C, but with respect to a sample which was formed with a butt weld in a double gated mold. The sample was unnotched, and it was placed in the vise so that the weld was coincident with the top surface of the vise jaws;

"(4) Dart Drop" is the Gardner dart drop impact test, which was performed at room temperature by dropping a 16 pound (7.26 km) weight, carrying a ½" (12.7 mm) dart, onto a circular test sample which was 2½" (63.5 mm) in diameter and 1/8" (3.175 mm) thick. The weighted dart fell freely on a slotted track and impacted the sample, which was secured in position in the path of descent on an aluminum cast base with a 0.640 inch (16.26 mm) hole to accept the dart after it impacted the sample. The instrument was a Pacific Scientific model no. IG-1120. The sample failed if it showed a crack or perforation on the side opposite from that on which impact occurred. The results are either pass (no break or perforation by the dart at the point of impact) or

fail (material exhibits crack or perforation) when the dart has developed a particular amount of energy by falling from the necessary height on the track, as indicated thereon, to develop such energy. The result appearing in Table III is the greatest amount of energy a sample could accept without failing;

"(5) Flexural Modulus" is flexural modulus as measured in accordance with ASTM Designation D 790-84a.

"(6) Retention of Elongation" is evaluated with respect to (a) samples which were (i) annealed at 250°F for thirty minutes, (ii) placed under 0.5 percent strain while submerged in a bath of 60 wt percent isooctane and 40 wt percent toluene for 5 minutes, and (iii) allowed to dry for 24 hours before testing; and (b) annealed samples which were not soaked in the solvent bath. Percent elongation at break, in accordance with ASTM Designation D 638-84, was measured with respect to each kind of sample, and a ratio was formed containing the elongation of the solvent-treated sample in the numerator and the elongation of the untreated sample in the denominator. This ratio is expressed as a percentage, and is reported as the portion (*i.e.* percentage) of the elongation of the untreated sample that was retained by, and thus possessed as a property of, the solvent-treated sample, after the solvent bath. Where the percentage reported exceeds 100, the solvent-soaked sample showed greater elongation at break than the untreated sample.

Table III

Test Results of Controls A-H

	A	B	C	D	E	F	G	H
(1) DTUL, °F	331	329	321	325	191	328	303	328
(2) Izod, ft-lb/in	4.3	1.5	3.3	2.5	1.5	1.2	3.5	1.1
(3) Weldline Izod, ft-lb/in	0.8	4.2	2.3	2.1	3.0	4.0	1.3	1.9
(4) Dart Drop, in-lb	400	290	450	300	<50	350	450	450
(5) Flexural Modulus, psi x 10^5	3.18	3.30	3.79	2.67	1.98	2.71	3.06	4.27
(6) Retention of Elongation	--	--	128	--	--	104	--	--

The results of the tests performed on Controls A-H demonstrate that neither a polyphenylene ether nor an elastomeric impact modifier alone was sufficient to relieve the brittle condition of a blend of a high heat polycarbonate and a polyester. Controls A-G all contain one or more elastomeric impact modifiers but no polyphenylene ether. Control H contains polyphenylene ether but no elastomeric impact modifier. The blended formulations of Controls A-H were all high heat materials, as can be seen from the respective DTUL results, but they were all also brittle, as can be seen respectively from the undesirably low Izod impact results.

The formulations of the polycarbonate compositions of Examples 1-8 are given below in Table IV in parts by weight of the total composition. In Table IV, all references are to the same materials used in Controls A-H, as described above, except that "(9) PA-2130" is a core-shell graft polymer containing 75 percent rubber, available from M&T Chemical Co., wherein styrene and methyl methacrylate are grafted onto a butadiene core.

The tests performed on Controls A-H were also performed on Examples 1-8. The results of those tests are shown below in Table V.

Table IV

Content of Examples 1-8 in Parts by Weight

	1	2	3	4	5	6	7	8
(1) Bisphenol AP PC	1,200	1,200	1,200	1,100	800	800	--	--
(2) Brominated PC I	--	--	--	--	--	--	1,200	--
(3) Brominated PC II	--	--	--	--	--	--	--	1,150
(4) Polyester	500	500	500	500	750	800	500	500
(5) Polyphenylene Ether I	100	100	100	100	200	100	100	150
(6) Kraton™G 1651	200	--	--	100	--	50	--	200
(7) E/VA/GMA	--	--	200	200	250	200	200	
(8) GRC 120	--	--	--	--	--	50		--
(9) PA 2130	--	200	--	--	--	--	--	--

Table V

Test Results of Examples 1-8

	1	2	3	4	5	6	7	8
(1) DTUL, °F	326	319	336	325	288	277	327	242
(2) Izod, ft-lb/in	9.0	8.4	9.6	7.5	3.2	5.6	1.6	10.1
(3) Weldline Izod, ft-lb/in	3.6	7.8	13.0	5.9	5.9	10.6	3.8	1.6
(4) Dart Drop, in-lb	500	400	475	425	300	250	400	450
(5) Flexural Modulus, psi x 10^5	3.33	3.73	3.61	2.54	2.86	2.41	2.81	2.77
(6) Retention of Elongation	87	--	128	108	--	82	110	--

The formulations of the polycarbonate compositions of Control J and Examples 9-12 are given below in Table VI in parts by weight of the total composition. In Table VI, all references are to the same materials used in Controls A-H, as described above. Three of the same tests performed on Controls A-H were performed on Control J and Examples 9-12. The results of those tests are also shown below in Table VI.

Table VI
Content in Parts by Weight, and Test Results,
for Control J and Examples 9-12

	J	9	10	11	12
(1) Bisphenol-AP PC	1,200	1,200	1,200	1,200	1,200
(4) Polyester	600	580	540	500	460
(5) Polyphenylene Ether I	- -	20	60	100	140
(6) Kraton™G 1651	200	200	200	200	200
(1) DTUL, °F	326	326	326	326	326
(2) Izod, ft-lb/in	3.6	10.0	8.8	8.8	8.8
(4) Dart Drop, in-lb	464	496	520	528	528

The results of the tests performed on Examples 1-12 demonstrate that when both a polyphenylene ether and an elastomeric impact modifier were admixed with a blend of a high heat polycarbonate and a polyester, desirably high DTUL was preserved while desirably high Izod impact value was attained - a balance of desirable properties. For instance, Examples 1-4 and 8-12 all had a DTUL which clearly indicated a high heat material - a material with superior resistance to thermal deformation, but they also had an Izod impact value which clearly indicated that the material was ductile. Examples 5 and 6 showed improved DTUL over the corresponding control with high polyester content, and Example 7 showed a composition with extremely favorable heat and solvent resistance.

The formulations of the polycarbonate compositions of Examples 13-21 are given below in Table VII in parts by weight of the total composition. In Table VII, all references are to the same materials used in Controls A-H, as described above, except that:

"(10) Polyphenylene Ether II" is Noryl™ N190 polyphenylene ether/styrenic polymer alloy, having a DTUL of 190°F, available from General Electric Company; and

"(11) Polyphenylene Ether III" is Noryl™ N225 polyphenylene ether/styrenic polymer alloy, having a DTUL of 225°F, available from General Electric Company.

Three of the tests performed on Controls A-H were also performed on Examples 13-21. The results of those tests are shown below in Table VIII.

Table VII

Content of Examples 13-21 in Parts by Weight

	13	14	15	16	17	18	19	20	21
(1) Bisphenol-AP PC	1,120	1,120	1,120	1,120	1,120	1,120	1,120	1,120	1,120
(4) Polyester	600	600	600	600	600	600	600	600	600
(5) Polyphenylene Ether I	--	--	--	--	--	--	100	140	180
(6) Kraton™G 1651	180	140	100	180	140	100	180	140	100
(10) Polyphenylene Ether II	100	140	180	--	--	--	--	--	--
(11) Polyphenylene Ether III	--	-	--	100	140	180	--	--	--

Table VIII

Test Results of Examples 13-21

	13	14	15	16	17	18	19	20	21
(1) DTUL, °F	304	314	305	306	316	303	314	322	319
(2) Izod, ft-lb/in	13.6	11.0	3.1	12.6	12.0	3.7	10.1	14.6	9.6
(6) Retention of Elongation	107	83	80	92	106	106	93	88	100

The formulations of the polycarbonate compositions of Control K and Examples 22-24 are given below in Table IX in parts by weight of the total composition. In Table IX, all references are to the same materials used in Controls A-H, as described above, except that:

"(12) Fluorene PC" is a polycarbonate having a T_g of 240°C and a weight average molecular weight of 22,500, prepared from mixture of Bis(hydroxyphenyl)Fluorene ("Bis-Fluorene") and Bisphenol-A ("Bis-A") in a 1.5/1 Bis-Fluorene/Bis-A molar ratio; and

"(13) Co-Polyester/PC" is a co-polyester/polycarbonate prepared from iso- and/or terephthalic acid (and/or derivatives thereof) and Bisphenol-A ("Bis-A") in a 3/1 acid/Bis-A ratio, having a T_g of 185°C and a weight average molecular weight of 29,000.

Three of the tests performed on Controls A-H were also performed on Control K and Examples 22-24, except the Izod impact test performed on Control K and Examples 22 and 23 was performed at 75°F, 100°F and 125°F. The results of those tests are shown below in Table X.

Table IX
Content of Control K and
Examples 22-24 in Parts by Weight

	K	22	23	24
(4) Polyester	600	540	600	600
(5) Polyphenylene Ether I	--	140	140	140
(6) Kraton™ G 1651	160	160	160	160
(12) Fluorene PC	1,240	1,160	1,100	--
(13) Co-Polyester/PC	--	--	--	1,100

Table X

Test Results of Control K

and Examples 22-24

	K	22	23	24
(1) DTUL, °F	394	376	381	286
(2) Izod, 75°F, ft-lb/in	1.9	3.5	4.1	10.5
(2) Izod,100°F, ft-lb/in	3.0	5.0	8.5	--
(2) Izod, 125°F, ft-lb/in	3.8	9.4	9.0	--
(4) Dart Drop, in-lb	--	512	464	--

The results of the tests performed on Examples 13-24 demonstrate that frequently very low amounts of polyphenylene ether are effective together with an impact modifier to reduce the brittleness of a blend of a high heat polycarbonate and a polyester. In addition, Examples 13-22 showed desirably high levels of solvent resistance.

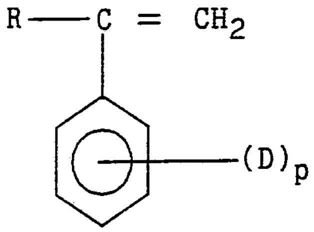
WHAT IS CLAIMED IS:

1. A composition of matter comprising, in admixture, (a) an aromatic polycarbonate which has a glass transition temperature in excess of at least 165°C, (b) an aromatic polyester, (c) a polyphenylene ether, and (d) an elastomeric impact modifier.

2. The composition of Claim 1 wherein the aromatic polycarbonate has a weight average molecular weight of less than 40,000.

3. The composition of Claim 1 wherein the polycarbonate is prepared from one or more dihydroxy compounds selected from (a) Tetrahalo Bisphenol-A, (b) Bisphenol-AP, (c) Bis(hydroxyphenyl)Fluorene, and (d) a mixture of one or more of the foregoing with one or more other bisphenols.

4. The composition of Claim 1 wherein the polyphenylene ether is blended with up to 50 percent, by weight of the polyphenylene ether, of a styrenic polymer or copolymer which contains at least 25 percent by weight of structural units derived from a monomer of the formula



wherein R is hydrogen, lower alkyl or halogen, D is vinyl, halogen or lower alkyl, and p is from 0 to 5.

5. The composition of Claim 1 wherein the elastomeric impact modifier is one or more of the members of the group consisting of a thermoplastic elastomer, a core-shell grafted copolymer and an olefinic elastomer.

6. The composition of Claim 5 wherein the thermoplastic elastomer is an A-B-A or A-B block copolymer which has a rigid block "A" having a glass transition temperature above the range of 23-25°C, and a rubbery block "B" having a glass transition temperature below the range of 23-25°C.

7. The composition of Claim 6 wherein the block "A" is polymerized from a vinyl aromatic compound and the block "B" is polymerized from an olefin or diene.

8. The composition of Claim 5 wherein the core-shell grafted copolymer is characterized in that

(a) it comprises greater than 40 percent rubber by weight,

(b) its core comprises a conjugated diene or of a C_1-C_{15} acrylate, said core having a glass transition temperature below 0°C, and

(c) its grafted phase comprises a carboxylic acid ester of a saturated aliphatic alcohol, acrylic or methacrylic acid, a vinyl nitrile compound, a vinyl aromatic compound, or a mixture thereof.

9. The composition of Claim 5 wherein the olefinic elastomer is a polymer which has a glass transition temperature less than 0°C, and which comprises

(a) (i) an olefin monomer, or (ii) a copolymer containing a sufficient amount of an olefin monomer to impart a glass transition temperature of less than 0°C to the polymer; and

(b) at least one vinyl monomer carrying at least one epoxide group.

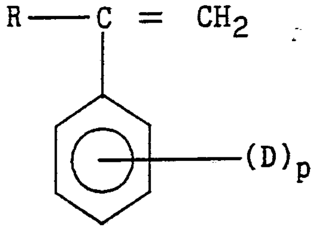
10. The composition of Claim 9 wherein the olefinic elastomer further comprises at least one vinyl monomer not carrying an epoxide group.

11. A composition of matter comprising, in admixture,

(a) an aromatic polycarbonate which has a glass transition temperature in excess of at least 165°C, prepared from one or more dihydroxy compounds selected from (i) Tetrahalo Bisphenol-A, (ii) Bisphenol-AP, (iii) Bis(hydroxyphenyl)Fluorene, and (iv) a mixture of one or more of the foregoing with one or more other bisphenols;

(b) a poly(alkylene dicarboxylate);

(c) a polyphenylene ether blended with up to 50 percent, by weight of the polyphenylene ether, of a styrenic polymer or copolymer which contains at least 25 percent by weight of structural units derived from a monomer of the formula



wherein R is hydrogen, lower alkyl or halogen, D is vinyl, halogen or lower alkyl, and p is from 0 to 5; and

(d) one or more elastomeric impact modifiers selected from the group consisting of

(i) an A-B-A or A-B block copolymer which has a rigid block "A" having a glass transition temperature above the range of 23-25°C, and a rubbery block "B" having a glass transition temperature below the range of 23-25°C;

(ii) a core-shell grafted copolymer characterized in that (A) it comprises greater than 40 percent rubber by weight, (B) its core comprises a conjugated diene or of a C_1-C_{15} acrylate, said core having a glass transition temperature below 0°C, and (C) its grafted phase comprises a carboxylic acid ester of a saturated aliphatic alcohol, acrylic or methacrylic acid, a vinyl nitrile compound, a vinyl aromatic compound, or a mixture thereof;

(iii) a polymeric olefinic elastomer which has a glass transition temperature less than 0°C, comprising (A) (I) an olefin monomer, or (II) a copolymer containing a sufficient amount of an olefin monomer to impart a glass transition temperature of less than 0°C to the polymer; and (B) at least one vinyl monomer carrying at least one epoxide group;

(iv) an ethylene/propylene/diene copolymer; and

(v) a nitrile rubber.

12. The composition of Claim 11 wherein component (a), the aromatic polycarbonate, has a weight average molecular weight of less than 40,000.

13. The composition of Claim 11 wherein component (d)(iii), the polymeric olefinic elastomer, further comprises at least one vinyl monomer not carrying an epoxide group.

14. The composition of Claim 1 or 11 in the form of a molded article.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/01545

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08L69/00; C08L67/02; C08L71/12; C08L57/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08L

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	EP,A,0 283 837 (GENERAL ELECTRIC COMPANY) 28 September 1988 see page 9, line 7 - line 25; claims 1,5-13 ---	1,3-11, 13,14
X	EP,A,0 306 774 (GENERAL ELECTRIC COMPANY) 15 March 1989 see claims 1-26 ---	1,3-5, 9-11,13, 14
A	EP,A,0 147 653 (BORG-WARNER CHEMICALS INC.) 10 July 1985 see claims 1-9 ---	1,5-11

° Special categories of cited documents : [10]

"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 principle 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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 01 JULY 1992	Date of Mailing of this International Search Report - 9. 07. 92
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer DECOCKER L.

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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9201545 SA 58208

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 01/07/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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