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(54) Titre : COMPOSITION DE MOULAGE THERMOPLASTIQUE A RESISTANCE AMELIOREE AUX CHOCS
(54) Title: IMPACT MODIFIED THERMOPLASTIC MOLDING COMPOSITION

(57) Abrégé/Abstract:
The impact strength of a thermoplastic molding composition containing aromatic polycarbonate resin and a copolymer is improved upon the incorporation therewith of a particular silicone rubber powder. The silicone rubber powder, added at a level of about 3 to 25 percent, contains a mixture of (a) a polydiorganosiloxane and (b) finely divided silica filler.

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IMPACT MODIFIED THERMOPLASTIC MOLDING COMPOSITION

ABSTRACT OF THE DISCLOSURE

The impact strength of a thermoplastic molding composition containing aromatic polycarbonate resin and a copolymer is improved upon the incorporation therewith of a particular silicone rubber powder. The silicone rubber powder, added at a level of about 3 to 25 percent, contains a mixture of (a) a polydiorganosiloxane and (b) finely divided silica filler.

IMPACT MODIFIED THERMOPLASTIC MOLDING COMPOSITION

BACKGROUND OF THE INVENTION

The invention concerns thermoplastic molding composition and more particularly a composition containing an aromatic polycarbonate resin.

The invention is based on the surprising and unexpected finding that the impact performance of a thermoplastic composition containing aromatic polycarbonate resin and a specific copolymer exemplified by styrene-acrylonitrile is improved upon incorporation therewith of a particular silicone rubber powder. The silicone rubber powder, added at a level of about 3 to 25 percent, relative to the weight of the composition, is characterized in that it contains a mixture of (a) a polydiorganosiloxane and (b) silica.

Thermoplastic aromatic polycarbonate resin is well known and is readily available in commerce. While the impact resistance of polycarbonate makes this resin the material of choice in a variety of demanding applications, attempts at improving this property continue. The literature includes a large number of patents directed to this subject.

Of particular relevance in the present context is a paper by R. Buch et al "Silicone-Based Additives for Thermoplastic Resins Providing Improved Impact Strength, Processing and Fire Retardant Synergy". This prior art paper (Dow Corning Corporation) disclosed certain silicone powder resin modifier products termed RM 4-7081* and RM 4-7051* to be useful in reducing the rate of heat release and the evolution rates of smoke and carbon monoxide of burning plastics, including polycarbonate. The relevant properties of compositions containing 99 and 95% polycarbonate, the balance in each composition being RM 4-7081,* are reported. Also disclosed is the impact strength improvement for engineering resins such as polyphenylene ether (PPE)

*trade-mark

and PPS. Improved impact strength of polycarbonate compositions is not reported.

Also related is Canadian Patent Application 2,083,014 which disclosed the silicone rubber powder of the present invention as a component in a composition containing poly(phenylene ether) resin.

Polycarbonate molding compositions which contain additive amounts of organosiloxane compounds are known: JP 5,262,960 is said to disclose a low viscosity polycarbonate resin composition which contains organo siloxane and a catalyst. The composition is said to exhibit lower melt viscosity and improved fluidity and moldability without loss of mechanical properties; JP 5,086,278 is considered to disclose an organosiloxane compound and a catalyst as additives to a polycarbonate resin. EP 505,869 disclosed a polycarbonate composition containing a siloxane compound, characterized in its high dimensional stability. Polycarbonate compositions containing a cyclosiloxane compound were disclosed in U.S. Patent 3,751,519 to have good release properties. A thermal oxidative stabilized polycarbonate composition containing a hydrocarbonoxy siloxane compound has been disclosed in U.S. Patent 4,197,384. U.S. Patent 5,322,882 disclosed a composition having improved impact strength containing a polycarbonate/polyorganosiloxane copolymer.

The copolymer of the invention generally, and styrene-acrylonitrile copolymer in particular are well known resins readily available in commerce.

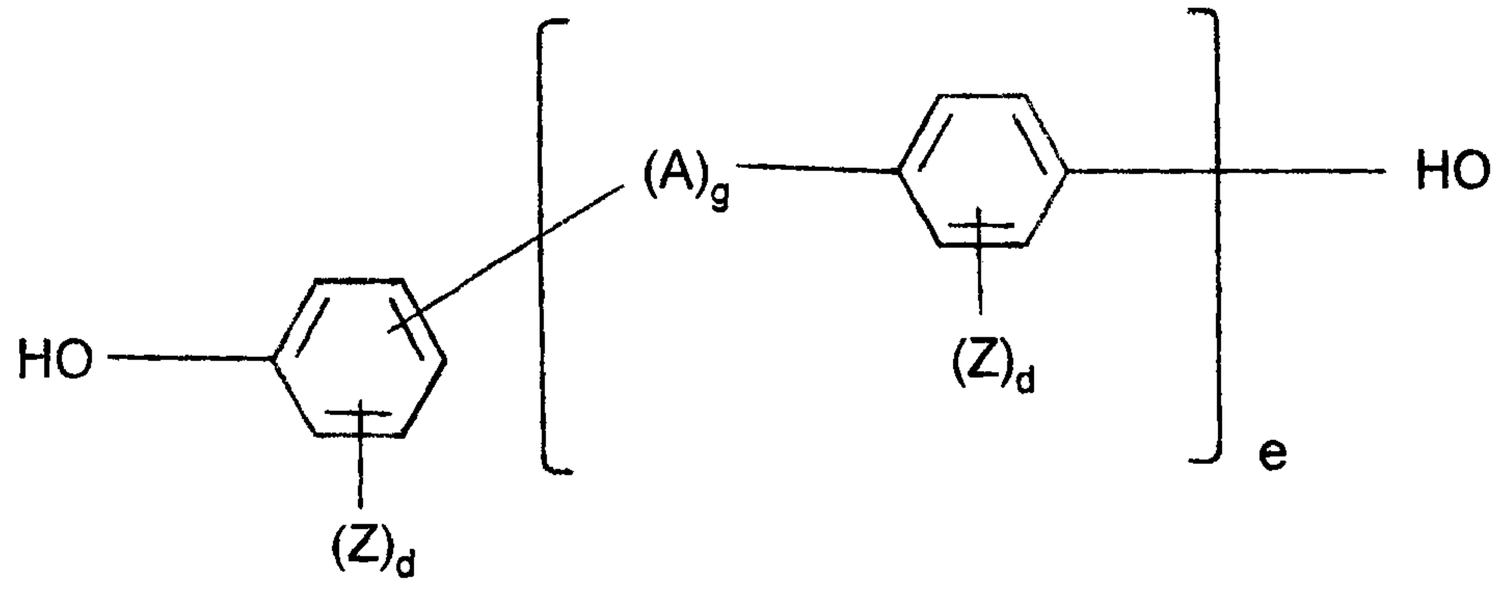
It has now been discovered that certain silicone rubber powders, preferably produced in accordance with the procedure disclosed in U.S. Patent 5,153,238 are useful as impact modifier in polycarbonate compositions which contain a copolymer of at least two ethylenically unsaturated monomers, preferably styrene-acrylonitrile copolymers. The inventive compositions therefore contain

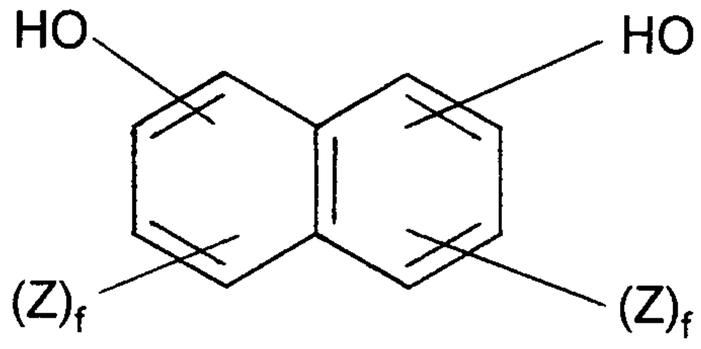
about 3 to 25, preferably 5 to 20 percent relative to the weight of the composition, of the silicone rubber powder.

The polycarbonate resins within the scope of the present invention include (co)polycarbonates and mixtures thereof.

The (co)polycarbonates generally have a weight average molecular weight of 10,000 to 200,000, preferably 20,000 to 80,000 and their melt flow rate, per ASTM D-1238 at 300°C, is about 1 to about 65 g/10 min., preferably about 2 to 15 g/10 min. They may be prepared, for example, by the known diphasic interface process from a carbonic acid derivative such as phosgene and dihydroxy compounds by polycondensation (see German Offenlegungsschriften 2,063,050; 2,063,052; 1,570,703; 2,211,956; 2,211,957 and 2,248,817; French Patent 1,561,518; and the monograph H. Schnell, "Chemistry and Physics of Polycarbonates", Interscience Publishers, New York, New York, 1964 .

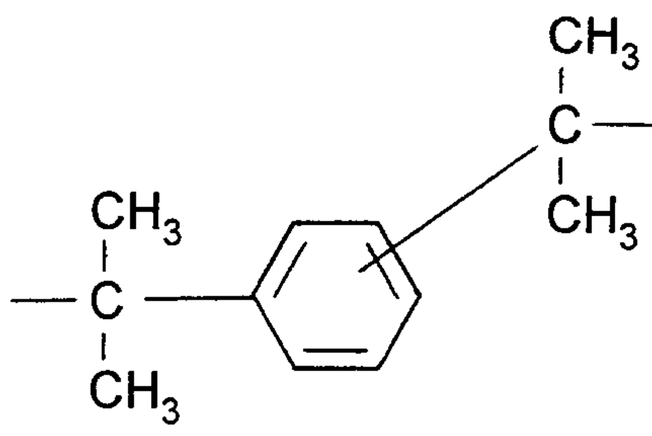
In the present context, dihydroxy compounds suitable for the preparation of the polycarbonates of the inventor conform to the structural formulae (1) or (2).





wherein

A denotes an alkylene group with 1 to 8 carbon atoms, an alkylidene group with 2 to 8 carbon atoms, a cycloalkylene group with 5 to 15 carbon atoms, a cycloalkylidene group with 5 to 15 carbon atoms, a carbonyl group, an oxygen atom, a sulfur atom, -SO- or -SO_2- or a radical conforming to



e and g both denote the number 0 to 1; Z denotes F, Cl, Br or C_1-C_4-alkyl and if several Z radicals are substituents in one aryl radical, they may be identical or different from one another; d denotes an integer of from 0 to 4; and f denotes an integer of from 0 to 3.

Among the dihydroxy compounds useful in the practice of the invention are hydroquinone, resorcinol, bis-(hydroxyphenyl)-alkanes, bis-(hydroxyphenyl)-ethers, bis-(hydroxyphenyl)-ketones, bis-(hydroxyphenyl)-sulfoxides, bis-(hydroxyphenyl)-sulfides, bis-(hydroxyphenyl)-sulfones, and α,α-bis-(hydroxyphenyl)-diisopropylbenzenes, as well as their nuclear-alkylated compounds. These and further suitable aromatic dihydroxy

compounds are described, for example, in U.S. Patents 3,028,356; 2,999,835; 3,148,172; 2,991,273; 3,271,367; and 2,999,846.

Further examples of suitable bisphenols are 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A), 2,4-bis-(4-hydroxyphenyl)-2-methylbutane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane, α,α'-bis-(4-hydroxyphenyl)-p-diisopropylbenzene, 2,2-bis-(3-methyl-4-hydroxyphenyl)-propane, 2,2-bis-(3-chloro-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-methane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfide, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfoxide, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfone, dihydroxybenzophenone, 2,4-bis-(3,5-dimethyl-4-hydroxyphenyl)-cyclohexane, α,α'-bis-(3,5-dimethyl-4-hydroxyphenyl)-p-diisopropylbenzene and 4,4'-sulfonyl diphenol.

Examples of particularly preferred aromatic bisphenols are 2,2,-bis-(4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane and 1,1-bis-(4-hydroxyphenyl)-cyclohexane.

The most preferred bisphenol is 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A).

The polycarbonates of the invention may entail in their structure units derived from one or more of the suitable bisphenols.

Among the resins suitable in the practice of the invention are included phenolphthalein-based polycarbonate, copolycarbonates and terpolycarbonates such as are described in U.S. Patents 3,036,036 and 4,210,741.

The polycarbonates of the invention may also be branched by condensing therein small quantities, e.g., 0.05 to 2.0 mol % (relative to the bisphenols) of polyhydroxyl compounds.

Polycarbonates of this type have been described, for example, in German Offenlegungsschriften 1,570,533; 2,116,974 and 2,113,374;

British Patents 885,442 and 1,079,821 and U.S. Patent 3,544,514. The following are some examples of polyhydroxyl compounds which may be used for this purpose: phloroglucinol; 4,6-dimethyl-2,4,6-tri-(4-hydroxy-phenyl)-heptane; 1,3,5-tri-(4-hydroxyphenyl)-benzene; 1,1,1-tri-(4-hydroxy-phenyl)-ethane; tri-(4-hydroxyphenyl)-phenylmethane; 2,2-bis-[4,4-(4,4'-dihydroxydiphenyl)]-cyclohexyl-propane; 2,4-bis-(4-hydroxy-1-isopropyl-idine)-phenol; 2,6-bis-(2'-dihydroxy-5'-methylbenzyl)-4-methylphenol; 2,4-dihydroxy-benzoic acid; 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)-propane and 1,4-bis-(4,4'-dihydroxytriphenylmethyl)-benzene. Some of the other polyfunctional compounds are 2,4-dihydroxy-benzoic acid, trimesic acid, cyanuric chloride and 3,3-bis-(4-hydroxyphenyl)-2-oxo-2,3-dihydroindole.

In addition to the polycondensation process mentioned above, other processes for the preparation of the polycarbonates of the invention are polycondensation in a homogeneous phase and transesterification. The suitable processes are disclosed in U.S. Patents 3,028,365; 2,999,846; 3,153,008; and 2,991,273.

The preferred process for the preparation of polycarbonates is the interfacial polycondensation process.

Other methods of synthesis in forming the polycarbonates of the invention such as disclosed in U.S. Patent 3,912,688 may be used.

Suitable polycarbonate resins are available in commerce, for instance, Makrolon* FCR, Makrolon* 2600, Makrolon* 2800 and Makrolon* 3100, all of which are bisphenol based homopolycarbonate resins differing in terms of their respective molecular weights and characterized in that their melt flow indices (MFR) per ASTM D-1238 are about 16.5 to 24, 13 to 16, 7.5 to 13.0 and 3.5 to 6.5 g/10 min., respectively. These are products of Bayer Corporation of Pittsburgh, Pennsylvania.

*trade-mark

A polycarbonate resin suitable in the practice of the invention is known and its structure and methods of preparation have been disclosed, for example in U.S. Patents 3,030,331; 3,169,121; 3,395,119; 3,729,447; 4,255,556; 4,260,731; 4,369,303 and 4,714,746.

The copolymers of the invention are characterized in that their weight average molecular weight (determined by light scattering or by sedimentation) is about 15,000 to 200,000 made of at least two ethylenically unsaturated monomers. The suitable monomers include vinyl aromatic hydrocarbons, such as styrene and halogen and/or alkyl substituted vinyl aromatics, exemplified by halogen and/or alkyl substituted styrene, acrylonitrile and substituted acrylonitrile, acrylate and alkyl substituted acrylates, methacrylates, alkyl substituted methacrylates and ethylenically unsaturated carboxylic acids, diacids, dianhydrides, acid esters, diacid esters, amides, imides and N-substituted imides.

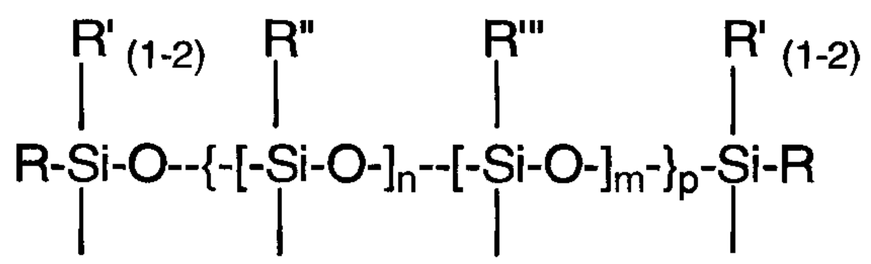
Preferred monomers include styrene, 3-methylstyrene; 3,5-diethylstyrene and 4-n-propylstyrene, α-methylstyrene, α-methyl-vinyltoluene, α-chlorostyrene, vinyltoluene, α-bromostyrene, chloro-phenylethylenes, dibromophenylethylenes, tetrachlorophenylethylenes, 1-vinylnaphthalene, 2-vinylnaphthalene, acrylonitrile, ethacrylonitrile, meth-acrylonitrile, α-chloroacrylonitrile, β-chloroacrylonitrile, α-bromoacrylo-nitrile and β-bromoacrylonitrile, methylacrylate, methylmethacrylate, ethylacrylate, butylacrylate, propylacrylate, isopropylacrylate, isobutyl-acrylate, and mixtures thereof. The preferred monovinyl aromatic hydrocarbon used herein is styrene and/or α-methylstyrene, acrylonitrile, ethylacrylate and methylmethacrylate. In a more preferred embodiment, the copolymer is formed from at least one first monomer selected from the group consisting of styrene, alpha methyl styrene, dibromostyrene and methyl methacrylate and at least one second, different monomer selected from the group consisting of acrylonitrile, methyl methacrylate,

maleic anhydride, maleimide, N-phenyl maleimide and acrylamide. Preferably, the first monomer forms about 60 to 95 percent, preferably 60 to 80 percent and the second monomer forms about 5 to 40 percent, preferably 20 to 40 percent relative to the weight of the copolymer. The preferred copolymer is styrene acrylonitrile (SAN).

The preparation of suitable copolymeric resins by radical polymerization, more especially by emulsion, suspension, solution or bulk polymerization is described in the literature. Suitable copolymers are readily available in commerce, including SAN copolymers which may be obtained from Monsanto under the trademark Lustran.

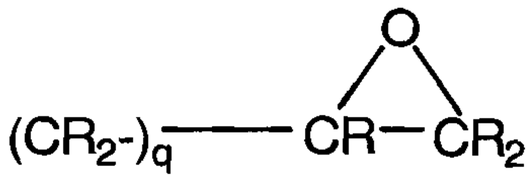
The silicone rubber powder of the invention has an average particle size of about 1 to 1000 microns and contains (i) 100 parts by weight (pbw) of a polydiorganosiloxane and (ii) about 10 to 80 pbw, preferably about 20 to 50 pbw of a finely divided silica filler.

The polydiorganosiloxane which is characterized in that its viscosity at 25°C is about 10^6 to 10^9 centipoise is a (co)polymeric resin having siloxane structural units represented by the general formula

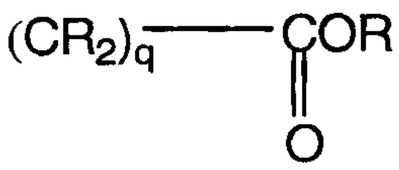


wherein R', R" and R'" independently denote hydrogen, C_{1-10}-alkyl, alkenyl, cycloalkyl radicals or aryl groups, preferably C_1-$_{10}$-alkyl, alkenyl, cycloalkyl radicals and aryl groups, and where p is about 1000 to 8000, preferably about 3000 to 6000 and where the relative weight proportions of n and m are 98.5 to 100:0 to 1.5, preferably 99:1, and where

X denotes a member selected from the group consisting of



and



where R denotes hydrogen, C_{1-10}-alkyl, alkenyl, cycloalkyl radicals or aryl groups, preferably C_{1-10}-alkyl, alkenyl, cycloalkyl radicals and aryl groups, and where q is 1 to 10.

The organic groups of the polydiorganosiloxane, which may optionally be halogenated, are preferably lower alkyl radicals containing 1 to 4 carbon atoms, phenyl and halogen substituted alkyl radicals. Examples include resins containing dimethylsiloxy units, phenylmethyl-siloxy units and dimethylsiloxy units and diphenyl siloxy units. Most preferably, the polydiorganosiloxane contains vinyl group(s) or epoxy group(s) at its chain termination(s) and/or along its main chain. The methods for the preparation of suitable polydiorganosiloxane are well known; a typical method comprises the acid- or base-catalyzed polymerization of cyclic diorganosiloxanes.

The silica filler required in the silicone rubber powder is a finely divided silica selected from among fumed silica and precipitated silica or silica gel. These are well known forms of silica and are readily available in commerce. The suitable silica is characterized in that its surface area is at least 50 m^2/g, preferably 50 to 900 m^2/g.

An additional embodiment entails use of treated silica which contains sites bonded to groups X as defined above; the manufacture of treated silica, typically by reacting the silanol groups on the silica surface

with about 1 to 2% by weight of an organic alkyl halide compound or an organosilicon halide compound, is known in the art.

Among the suitable compounds, mention may be made of low molecular weight liquid hydroxy- or alkoxy-terminated polydiorgano-siloxanes, hexaorganosiloxanes and hexaorganosilazanes.

The procedure for the preparation of the silicone rubber powder has been described in detail in U.S. Patent 5,153,238. Suitable silicone rubber powder is available in commerce from Dow Corning Corporation under the trademark RM 4-7051 and RM 4-7081.

The preparation of the composition of the invention is carried out following conventional procedures and by use of conventional means such as single, preferably twin screw extruders. Conventional thermo-plastic processes are suitable in molding useful articles from the inventive composition.

Compositions in accordance with the invention have been prepared following well-known conventional procedures and their properties were determined as described below: In Examples 1 through 6, the polycarbonate resin was Makrolon* 2600 resin, a Bayer product (a bisphenol-A based homopolycarbonate having a MFR of about 11 g/10 min. in accordance with ASTM D-1238 (@ 300°C under 1200 g load); in compositions 7 and 8, the polycarbonate was Makrolon*6030, a copolycarbonate of brominated bisphenol-A, having a MFR of about 4 g/10 min. and containing about 5.5% of bromine. In all the examples, the copolymer was Lustran* SAN33, a product of Monsanto (72% styrene and 28% acrylonitrile). The silicone rubber powder was Dow Corning's RM 4-7051*.

*trade-mark

Table 1

Example	1	2	3	4	5	6
polycarbonate, wt%	65	62	60	80	73.6	68
SAN, wt%	35	35	32	20	18.4	17
silicone rubber powder, wt%	0	3	8	0	8	15
Impact strength, Notched Izod						
1/8" ft.lb/inch	0.3	1.0	1.0	1.3	4.6	5.6

In Examples 7 and 8, the polycarbonate resin used was a copolycarbonate of BPA and bromine-substituted BPA. Both compositions contained as a flame retarding package, triphenyl phosphate and PTFE, neither of which are critical to the invention. The SAN and silicone rubber powder were as noted above.

Table 2

Example	7	8
copolycarbonate, wt%	79.2	72.1
SAN, wt%	13.8	12.5
silicone rubber powder, wt%	0	8.9
Impact strength, Notched Izod		
1/8" ft.lb/inch	0.4	9.0

The finding giving rise to the invention were supplemented by Example 9 where a SAN-rich composition (55% SAN, 30% polycarbonate and 15% silicon rubber powder) show no advantages in terms of impact strength.

Conventional additives may be incorporated in the composition of the invention in the usual quantities. Mention may be made of a thermal stabilizer, a mold release agent, a pigment, a flame retarding agent, a uv stabilizer, a hydrolysis stabilizer, a gamma radiation stabilizer and a

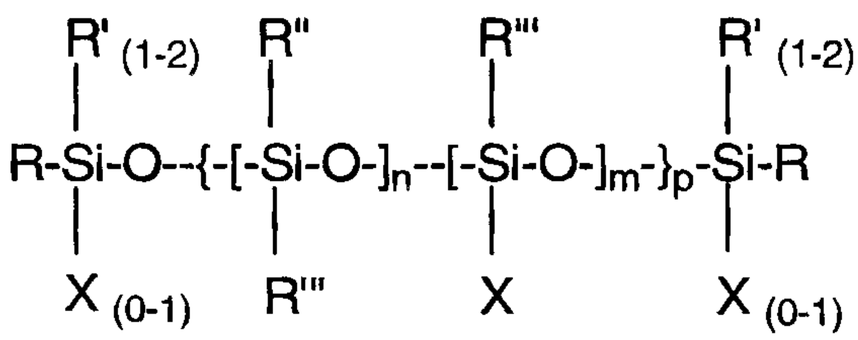
plasticizer for polycarbonate compositions, as well as fillers and reinforcing agents such as glass fibers.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

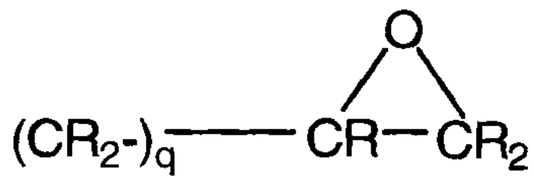
CLAIMS:

1. A thermoplastic molding composition comprising (a) about 60 to 96% aromatic polycarbonate resin, (b) about 1 to 35% copolymer of at least two ethylenically unsaturated monomers and having weight average molecular weight (determined by light scattering or by sedimentation) of about 15,000 to 200,000, and (c) about 3 to 25% silicone rubber powder, said percent being relative to the weight of the composition, said silicone rubber powder having an average particle size of about 1 to 1000 microns and containing

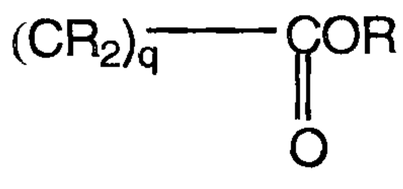
(i) 100 pbw of a polydiorganosiloxane having a viscosity at 25°C is about 10^6 to 10^9 centipoise and siloxane structural units represented by the general formula



wherein R', R" and R'" independently denote a member selected from the group consisting of hydrogen atom, C_{1-10}-alkyl, alkenyl, cycloalkyl radicals and aryl groups, and where p is about 1000 to 8000 and where the relative weight proportions of n and m is 98.5 to 100:0 to 1.5, and where X denotes a member selected from the group consisting of



and



where R denotes a member selected from the group consisting of hydrogen, C_{1-10}-alkyl, alkenyl, cycloalkyl radicals or aryl groups and where q is 1 to 10, and

(ii) about 10 to 80 pbw of a finely divided silica selected from a group consisting of fumed silica, precipitated silica and silica gel having a surface area of at least 50 m^2/g,

said composition characterized in that it has a notched Izod impact strength value which is greater than that of the composition in the absence of said silicon rubber powder.

2. The composition of Claim 1 wherein each of said R, R', R" and R'" is independently selected from the group consisting of C_{1-10}-alkyl; alkenyl; cycloalkyl; and aryl groups.

3. The composition of Claim 2 wherein each of said R, R', R" and R'" is independently selected from the group consisting of alkyl radical containing 1 to 4 carbon atoms and phenyl radical.

4. The composition of Claim 1 wherein said silica has a surface area of about 50 to 900 m^2/g.

5. The composition of Claim 1 wherein said p is about 5000 to 6000.

6. The composition of Claim 1 wherein the relative weight proportions of n and m is 99:1.

7. The composition of Claim 1 wherein said finely divided silica is treated silica which contains sites bonded to said X.

8. The composition of Claim 1 further containing at least one member selected from the group consisting of a thermal stabilizer, a mold release agent, a pigment, a flame retarding agent, a uv stabilizer, a hydrolysis stabilizer, a gamma radiation stabilizer, a plasticizer, a filler and a reinforcing agent.

9. The composition of Claim 1 wherein said copolymer of at least two ethylenically unsaturated monomers is styrene-acrylonitrile copolymer.

10. The composition of Claim 9 wherein said silica has a surface area of about 50 to 900 m^2/g.

11. The composition of Claim 9 wherein the relative weight proportion of n and m is 99:1.