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(57) Abstract

A thermoplastic molding composition suitable for preparing molded articles having improved properties, most notably high ductility and impact strength at low temperature, is disclosed. The composition contains a resinous blend of aromatic polycarbonate and a mixture of at least two grafted rubbers. The mixture of grafted rubbers contains a "small-mode" component having a weight average particle size of less than 0.3 microns and a "large-mode" component having a weight average particle size of 0.3 microns or larger.

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COMPOSITIONS CONTAINING POLYCARBONATE AND GRAFTED RUBBER HAVING IMPROVED LOW-TEMPERATURE TOUGHNESS

FIELD OF THE INVENTION

The present invention relates to a thermoplastic molding composition and more particularly to a composition containing polycarbonate and grafted rubber.

SUMMARY OF THE INVENTION

A thermoplastic molding composition suitable for preparing molded articles having improved properties, most notably high ductility and impact strength at low temperature, is disclosed. The composition contains a resinous blend of aromatic polycarbonate and a mixture of at least two grafted rubbers. The mixture of grafted rubbers contains a "small-mode" component having a weight average particle size of less than 0.3 microns and a "large-mode" component having a weight average particle size of 0.3 microns or larger.

TECHNICAL BACKGROUND OF THE INVENTION

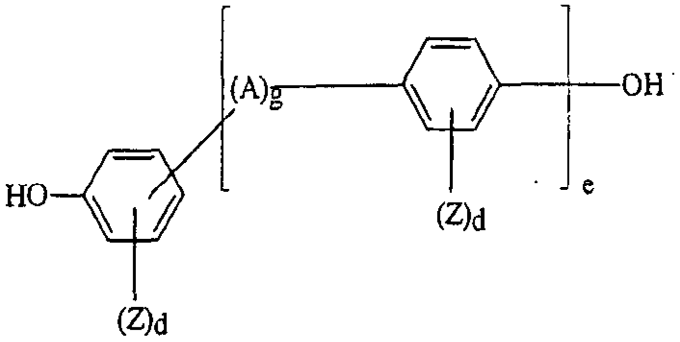
Thermoplastic molding compositions containing grafted rubber, such as ABS, and polycarbonate resin are known. Commercial products based on such compositions, notably Bayblend compositions that are available from Bayer Corporation, have long enjoyed wide market acceptance. U.S. Patents 3,954,905 and 4,560,725 are noted to have disclosed relevant compositions. Also known are compositions which include ABS components, the rubber particles of which conform to bimodal size distributions. The art is noted to include U.S. Patent 3,509,237 which disclosed a composition containing first and second graft copolymers having a rubber substrate and a superstrate of an interpolymer of a monovinylidene aromatic hydrocarbon and an unsaturated nitrile. The first and second graft copolymers have a number average particle size, of 0.8 to 2.0 microns and 0.01 to 0.25 microns respectively. The first graft is said to be a product of suspension polymerization and the second is produced by emulsion. U.S. Patent 4,677,162 is noted for its disclosed composition, which contains polycarbonate, a graft copolymer and an impact modifier. While the graft copolymer entails particles averaging more than 0.75 microns, the impact modifier entailed in the working examples embraces a second graft copolymer having presently relevant chemical makeup and particle size.

DETAILED DESCRIPTION OF THE INVENTION

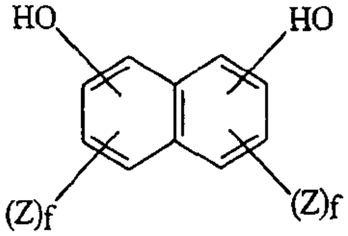
The inventive composition contains a resinous blend of about 60 to 80 percent polycarbonate resin and 20 to 40 percent of a mixture of at least two grafted rubbers. In a preferred embodiment, the blend contains 65 to 75 percent polycarbonate and 25 to 35 percent of the mixture; in all instances, the percents are in relation to the weight of the blend. The mixture of grafted rubbers contains a "small-mode" component (ABS-s) having a weight average particle size smaller than 0.3 microns, preferably about 0.15 to 0.28 microns, and a "large-mode" component (ABS-l), wherein weight average particle size is at least 0.3 micron, preferably about 0.35 to 0.65 micron. The weight ratio ABS-s/ABS-l in the mixture ranges from 3/27 to 7.5/22.5, preferably 3/27 to 5/25. In the preferred embodiments, ABS-s is a product of the well-known emulsion polymerization process and ABS-l is a product of the known mass, more preferably continuous mass, polymerization process.

The aromatic polycarbonate resins useful in the context of the present invention include homopolycarbonates and copolycarbonates and mixtures thereof. The suitable polycarbonates 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 24 g/10 min. These resins 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, all incorporated herein by reference).

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



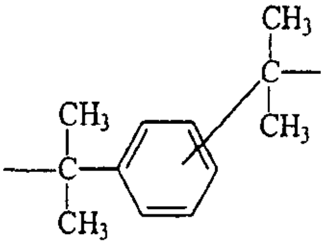
(1)



(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_{1-4}-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 5,126,428; 5,104,723; 5,041,521; 5,034,457; 3,028,356; 2,999,835; 3,148,172; 2,991,273; 3,271,367; and 2,999,846, all incorporated herein by reference.

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-diisopropyl-benzene 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 is included phenolphthalein-based polycarbonate, copolycarbonates and terpolycarbonates such as are described in U.S. Patents 3,036,036 and 4,210,741, both incorporated by reference herein.

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-hydroxyphenyl)-heptane; 1,3,5-tri-(4-hydroxyphenyl)-benzene; 1,1,1-tri-(4-hydroxyphenyl)-ethane; tri-(4-hydroxyphenyl)-phenylmethane; 2,2-bis-[4,4-(4,4'-dihydroxydiphenyl)]-cyclohexyl-propane; 2,4-bis-(4-hydroxy-1-isopropylidine)-phenol; 2,6-bis-(2'-dihydroxy-5'-methylbenzyl)-4-methylphenol; 2,4-dihydroxybenzoic 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-dihydroxybenzoic 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 the incorporated herein by reference, 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, incorporated herein by reference, may be used.

Suitable polycarbonate resins are available in commerce, for instance, Makrolon 2400, 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.

Polycarbonate resins suitable in the practice of the invention are known and their structures 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 all of which are incorporated by reference herein.

The mixture included in the inventive composition contains a "small-mode" component (ABS-s) having a weight average particle size smaller than 0.3 microns, preferably 0.15 to 0.28 micron, and a "large-mode" component (ABS-l) having a weight average particle size of at least 0.3 micron, preferably 0.35 to 0.65 micron. The weight ratio ABS-s/ABS-l in the mixture ranges from 3/27 to 7.5/22.5, preferably 3/27 to 5/25.

The grafted phase in both grafted rubber components of the instant mixture contains a monovinylidene aromatic hydrocarbon and an unsaturated nitrile. Such monomers comprise at least 50.0 percent by weight, preferably at least 75 percent by weight of the grafted phase. Most desirably, such monomers comprise at least 90 percent of the grafted phase. Minor amounts, preferably less than 10 percent of other comonomers may be included. Examples of the monovinylidene aromatic hydrocarbons which may be used in the preparation of the grafted phase include styrene, alpha-alkyl monovinylidene monoaromatic compounds, e.g., alpha-methylstyrene, alpha-ethylstyrene, alpha-methyl-vinyltoluene, alpha-methyl dialkylstyrenes, etc., ring-substituted alkyl styrenes, e.g., vinyl toluene, o-ethylstyrene, p-ethylstyrene, 2,4-dimethylstyrene, etc., ring-substituted halostyrenes, e.g., o-chlorostyrene, p-chlorostyrene, o-bromostyrene, 2,4-dichlorostyrene, etc., ring-alkyl, ring-halosubstituted styrenes, e.g., 2-chloro-4-methylstyrene, 2,6-dichloro-4-methylstyrene, etc., vinyl naphthalene; vinyl anthracene, etc. The alkyl substituents generally have 1 to 4 carbon atoms and may include isopropyl and isobutyl groups. If so desired, mixtures of such monovinylidene aromatic monomers may be employed.

Examples of the unsaturated nitriles, which may, singly or in combination one with the others, be used in the preparation of the grafted phase include acrylonitrile, methacrylonitrile, and ethacrylonitrile.

Examples of additional monomers which may be copolymerized in small amounts in the grafted phase include conjugated 1,3 dienes, e.g., butadiene, isoprene, etc.; alpha- or beta-unsaturated mono-basic acids and derivatives thereof, e.g., acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methacrylic acid and the corresponding esters thereof, acrylamide, methacrylamide; vinyl halides such as vinyl chloride, vinyl bromide, etc.; vinylidene chloride, vinylidene bromide, etc.; vinyl esters such as vinyl acetate, vinyl propionate, etc.; dialkyl maleates or fumarates such as dimethyl maleate, diethyl maleate, dibutyl maleate, the corresponding fumarates, etc.

The polymerizable monomer mixture forming the grafted phase contains at least 20 percent by weight of the monovinylidene aromatic monomer and preferably at least 50 percent by weight thereof. They also contain at least 5 percent by weight of the unsaturated nitrile and preferably at least 10 percent by weight thereof. From the standpoint of highly advantageous commercial practice, the monomer formulations contain 20 to 95 percent, and preferably 60 to 85 percent, by weight of the vinylidene aromatic hydrocarbon and 80 to 5 percent, and preferably 40 to 15 percent, by weight of the unsaturated nitrile.

The rubber substrate in both grafted rubber components onto which the grafted phase is grafted during the polymerization process and in the presence thereof is a diene rubber. These are prepared of one or more conjugated 1,3-dienes, such as, butadiene, isoprene, piperylene, chloroprene, etc. Such rubbers include homopolymers and interpolymers of conjugated 1,3-dienes with up to an equal amount by weight of one or more copolymerizable monoethylenically unsaturated monomers, such as monovinylidene aromatic hydrocarbons (e.g., styrene; an aralkyl-styrene, such as the o-, m-, and p-methylstyrenes, 2,4-dimethylstyrene, the ar-ethyl-styrenes, p-tert-butylstyrene, etc.; an alpha-alkylstyrene, such as alpha-methylstyrene, alpha-ethylstyrene, alpha-methyl-p-ethylstyrene, etc.; vinyl naphthalene, etc.); arhalo monovinylidene aromatic hydrocarbons (e.g., the o-, m-, and p-chlorostyrenes, 2,4-dibromostyrene, 2-methyl-4-chlorostyrene, etc.); acrylonitrile; methacrylonitrile; alkyl acrylates (e.g., methyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, etc.), the corresponding alkyl methacrylates; acrylamides (e.g., acrylamide, methacrylamide, N-butyl acrylamide, etc.); unsaturated ketones (e.g., vinyl methyl ketone, methyl isopropenyl ketone, etc.); alpha-olefins (e.g., ethylene, propylene, etc.); pyridines; vinyl esters (e.g., vinyl acetate, vinyl stearate, etc.); vinyl and vinylidene halides (e.g., the vinyl and vinylidene chlorides and bromides, etc.); and the like.

The rubber substrate may be crosslinked by the addition into the polymerizable mixture up to about 2 percent, relative to the weight of the rubber forming monomers, of a conventional crosslinking agent, such as divinylbenzene, diallyl meleate, diallyl fumerate, diallyl adipate, allyl acrylate, allyl methacrylate, diacrylates and dimethacrylates of polyhydric alcohols, such as ethylene glycol dimethacrylate.

A preferred group of rubbers are those consisting essentially of 75 to 100 percent by weight of butadiene and/or isoprene and up to 25 percent by weight of a monomer selected from the group consisting of monovinylidene aromatic hydrocarbons (e.g., styrene) and unsaturated nitriles (e.g., acrylonitrile), or mixtures thereof. Particularly advantageous substrates are butadiene homopolymer or an interpolymer of 90 to 95 percent by weight butadiene and 5 to 10 percent by weight of acrylonitrile or styrene.

Preferably, the ABS-s component of the invention is made by the known emulsion polymerization process. Its rubber substrate amounts to about 50 to 60% relative to its weight and the grafted phase is characterized in that the weight ratio of the polymerized monovinylidene aromatic hydrocarbons to the polymerized unsaturated nitriles is 70-80/30-20, preferably 75-78/25-22.

In the emulsion polymerization process, the monomers and rubber substrate are emulsified in water by use of suitable emulsifying agents such as fatty acid soaps, alkali metal or ammonium soaps of high molecular weight alkyl or alkaryl sulfates and sulfonates, mineral acid salts of long chain aliphatic amines, etc. Emulsifying agents which have proven particularly advantageous are sodium oleate, sodium palmitate, sodium stearate and other sodium soaps. Generally, the emulsifying agent is provided in amounts of about 1 to 15 parts by weight per 100 parts by weight of the monomers, and water is provided in an amount of about 1 to

4 parts per part of monomers, and even in larger ratios where greater dilution is desirable.

If so desired, aqueous latex formed in the emulsion polymerization of the rubber substrate may provide the aqueous medium into which the monomers are incorporated with or without additional emulsifying agents, etc. However, the rubber may be dissolved in the monomers and the mixture emulsified, or a latex thereof may be separately prepared.

Various water-soluble free radical polymerization initiators are conventionally used for emulsion polymerization of the rubber monomer including conventional peroxy and perazo catalysts and the resultant latex may be used as the aqueous medium with which the interpolymer monomers are admixed. In this manner, the catalyst for the rubber polymerization may function in whole or in part as the catalyst for the graft polymerization. However, additional catalyst may be added at the time of graft polymerization. Exemplary of suitable peroxy catalysts are the alkali metal peroxides, persulfates, perborates, peracetates, and percarbonates, and hydrogen peroxide. If so desired, the catalysts may be activated to form redox systems. In addition, it may be advantageous to include an oil-soluble catalyst such as those hereinbefore identified for mass-emulsion polymerization processes. However, other free-radical generating catalysts may be employed such as actinic radiation.

Chain transfer agents and other polymerization modifiers may desirably be included and it is generally advantageous to incorporate a higher alkyl mercaptan, such as tert-dodecyl mercaptan, which acts both as a promoter and a regulator. In addition, antioxidants and stabilizers such as the alkylated phenols may be added.

The emulsion mixture is then polymerized in an inert atmosphere at temperatures in the range of 20 to 100° centigrade with agitation. Pressures of 1 to 100 pounds per square inch may be employed and the monomers and/or additional catalyst may be added incrementally or continuously over a portion of the reaction cycle. Polymerization is continued until substantially all, i.e., more than 90 percent, of the monomers have reacted. The remaining monomers and other volatile components are then distilled from the latex, which is then dewatered, and dried.

The ABS-I component of the inventive composition is preferably made by the known mass, more preferably continuous mass polymerization process. The rubber in this graft copolymer is preferably butadiene or butadiene/styrene copolymer (90/10 by weight) and the rubber content is about 14 to 20% relative to the weight of the graft copolymer. The grafted phase is characterized in that the weight ratio of the polymerized monovinylidene aromatic hydrocarbons to the polymerized unsaturated nitriles is 73-80/27-20, preferably 75-78/25-22.

In the continuous mass polymerization process, the rubber substrate is initially dissolved in the monomers and the solution, initiator and any other optional components such as a solvent are continuously charged to a stirred or unstirred reactor which provides a continuous polymerization zone containing the polymerizing mixture with a substantially uniform composition throughout. A plurality of reactors may be employed in series with each operating in a continuous mode in which the polymerization is advanced to the required conversion. After polymerization has progressed to the desired conversion level, the residual monomer is stripped from the polymer. The devolatilizing operation, which is the same whether one or a series of polymerization reactors is employed, is conventionally done in a separate device such as a wiped film or falling strand devolatilizer.

Typical prior art processes for the continuous production of grafted rubbers by mass polymerization are described in U.S. Patents 3,243,481, 3,337,750, 3,511,895 and 4,417,030, the content of the latter being incorporated herein by reference.

The polymerization may be initiated by any free radical generating initiator that promotes grafting and is activated at the contemplated reaction temperatures. Suitable initiators comprise the conventional monomer-soluble peroxy and perazo compounds. Exemplary initiators are t-butyl-peroxy-neodecanoate, t-butyl-peroxy-2-ethylhexanoate, 1-t-butyl-azo-1-cyanocyclohexane, di-tert-butyl peroxide, benzoyl peroxide lauroyl peroxide, oleyl peroxide, toluyl peroxide, di-tert-butyl diperphthalate, tert-butyl peracetate, tert-butyl perbenzoate, dicumyl peroxide, tert-butyl peroxide isopropyl carbonate, 2,5-dimethyl-2,5-di-(tert-butylperoxy) hexane, 2,5-dimethyl-2,5-di-(tert-butylperoxy)-hexyne-3, tert-butyl hydroperoxide, bumene hydroperoxide, p-methane hydroperoxide, cyclopentane, hydroperoxide, diisopropylbenzene hydroperoxide, p-tert-butylcumene hydroperoxide, penant hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, as well as percarbonate compounds such as t-butyl-2-ethylhexyl-monoperoxycarbonate, etc. and mixtures thereof.

The initiator is generally included within the range of 0.001 to 1.0 percent by weight, and preferably on the order of 0.005 to 0.5 percent by weight of the polymerizable material, depending upon the monomers and the desired polymerization cycle.

It is often desirable to incorporate molecular weight regulators such as mercaptans, halides and terpenes in relatively small percentages by weight, on the order of 0.001 to 1.0% by weight of the polymerizable material. In addition, it may be desirable to include relatively small amounts of antioxidants or stabilizers such as the conventional alkylated phenols. Alternatively, these may be added during or after polymerization. The formulation may also contain other additives such as plasticizers, lubricants, colorants and non-reactive preformed polymeric materials which are suitable or dispersible therein.

A solvent or diluent can be used to dilute the reaction mixture to a point at which the power requirements for agitation in stirred reactor(s) are not excessive. Some or all of such diluents can be introduced with the rubber in monomer solution either as an added component or by use of a rubber which is already dissolved in a suitable solvent. Diluent can also be added separately to one or more of the reactors.

The diluents can be liquid aromatic hydrocarbons containing 6 to 10 carbon atoms, e.g., benzene, toluene, xylene, ethyl benzene, para cymene, cumene or mixtures thereof. Other organic solvents such as saturated aliphatic hydrocarbons, e.g., hexane, cyclohexane, cyclopentane and others having 5 to 7 carbon atoms, ketones, e.g., methyl ethyl ketone, methyl cyclopentane, methyl isobutyl ketone, cyclohexane or methyl propyl ketone can also be used. Methylethyl ketone is preferred.

A preferred continuous mass process for separately preparing ungrafted matrix copolymer is disclosed in U.S. Patent 3,813,369 which is incorporated herein by reference. In summary, the monomers are continuously charged to a well-mixed polymerization reaction zone comprising liquid and vapor phases. The liquid phase contains the monomer composition as a solvent in which copolymer being formed from the monomer composition is dissolved. The vapor phase above the liquid phase comprises the monomer composition. Liquid and vapor are continuously removed from the reaction zone and replenished by charging at a rate about equal to the rate at which the monomers are polymerized and removed. The removed vapor phase may be condensed by reflux condensation and returned to the reaction zone as part of the monomer composition being charged to the zone. The mixture of withdrawn polymer and monomer is passed through one or more devolatilizers of the type referred to above to separate out the polymer. The hot melt may then be pelletized in conventional apparatus while the separated monomer is condensed and returned to the reaction zone. Chain transfer agents and liquid solvents, initiators, and other additives of the type described above with respect to the continuous mass graft polymerization process may be charged continuously with the monomer composition or separately to the reaction zone.

The average particle size of a rubber graft copolymer - i.e., the rubber substrate and its graft copolymer superstrate, is based upon the average of the particles of the several sizes in each rubber graft copolymer component. Particle size is measured using a photosedimentometer by the published procedure of Graves, M. J. et. al. "Size Analysis of Subsieve Powders Using a Centrifugal Photosedimentometer", British Chemical Engineering 9:742- 744 (1964). Alternatively an electron microscope may be used.

The inventive composition may be prepared and processed conventionally by means and the following procedures that are well known to the art-skilled.

EXAMPLES

Compositions demonstrating the invention have been made and their properties were determined. The table below summarizes the results of the evaluation. In preparing the composition, the following components were used:

Polycarbonate: a homopolycarbonate based on bisphenol A, having a melt flow rate of about 11 gm/10 min. as determined in accordance with ASTM D-1238.

ABS-l (a): a graft copolymer containing 16% butadiene/styrene (90/10 wt.%) rubber and having the ratio of S/AN of 77/23, having a particle size, weight average, of 0.64 microns.

ABS-l (b): a graft copolymer containing 16% butadiene/styrene (90/10 wt.%) rubber and having the ratio of S/AN of 77/23, having a particle size, weight average, of 0.35 microns.

ABS-s: a graft copolymer containing 53% butadiene rubber, and having SAN ratio of 73/27 and a weight average particle size of 0.28 microns.

SAN: a copolymeric phase having a ratio of styrene/acrylonitrile of 72.5/27.5.

The Vicat temperature was determined in accordance with ASTM 1525; Izod impact strength, in accordance with ASTM D 256; Multiaxial impact strength, in accordance with ASTM D3763 (test velocity 6.7 m/s; striker mass selected to minimize velocity loss during impact.) Ductility: the definition of ductile failure for the examples presented in the table below, is based on General Motors Engineering standard GMP.ABS+PC.002. Using the multiaxial impact test, a test specimen is deemed to have exhibited ductile failure if the puncture of the test specimen is accompanied by cracks radiating no more than 10 mm beyond the center of the impact point. The reported ductile failures denote the percents of the specimens failed in this fashion, out of the fifteen specimens tested.

The compositions also contained a mold release agent and an antioxidant in conventional amounts, having no criticality in the context of the invention. The compositions of the invention (represented by Examples 1, 2, 3 and 4) are set in comparison to a corresponding composition, Example 5, which although containing a corresponding amount of rubber and exhibits largely identical or better Vicat properties and Izod impact strength, is characteristically more brittle at low temperature than are the inventive compositions.

	1	2	3	4	5 (Com.)
Polycarbonate	70	70	70	70	70
ABS-I(a)	30	27			
ABS-I(b)			30	27	
ABS-s		3		3	13
SAN					17
Total Rubber	4.8	5.91	4.8	5.91	6.89
Properties					
Vicat temperature (°C) 1Kg@120°C/hr	144	144.9	144.2	144.3	145
Impact Strength, Izod (ft-lb/in)					
1/8" At 23°C	11.7	10.9	10.9	11	11.5
1/8" At -30°C	5.3	7.1	5.7	7.8	9
multiaxial Impact strength, at -30°C (J)					
(Emax)	50	56	52	51	46
(Efail)	55	60	56	56	48
Brittle/Ductile	9/6	1/14	10/5	2/13	10/0
Ductile failures, percent	40	93	33	87	0

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.

WHAT IS CLAIMED IS:

1. A thermoplastic molding composition comprising a blend of

(i) 60 to 80 percent polycarbonate resin and

(ii) 20 to 40 percent of a mixture of at least two grafted rubbers,

said percents being in relation to the weight of the blend, wherein mixture contains a small-mode component containing a grafted rubber having a particle size, weight average, smaller than 0.3 micron and a large-mode component containing a grafted rubber having a particle size, weight average of at least 0.3 microns, said mixture further characterized in that said small-mode component and large mode component are present in the blend at a weight ratio of 3/27 to 7.5/22.5 therebetween.

2. The thermoplastic molding composition of Claim 1 wherein said blend contains 65 to 75 percent polycarbonate and 25 to 35 percent of said mixture.

3. The thermoplastic molding composition of Claim 1 wherein said range is 3/27 to 5/25.

4. The thermoplastic molding composition of Claim 1 wherein said small mode component is a product of emulsion polymerization.

5. The thermoplastic molding composition of Claim 1 wherein said large mode component is a product of mass polymerization.

6. The thermoplastic molding composition of Claim 1 wherein said large mode component is a product of continuous mass polymerization.

7. The thermoplastic molding composition of Claim 1 wherein small-mode component has a particle size, weight average, of 0.15 to 0.28 microns.

8. The thermoplastic molding composition of Claim 1 wherein said large-mode component has a particle size, weight average, of 0.35 to 0.65 microns.

9. The thermoplastic molding composition of Claim 1 wherein said small mode component contains rubber at an amount of 50 to 60% relative to its weight.

10. The thermoplastic molding composition of Claim 9 wherein said small mode component contains a grafted phase, polymerized monovinylidene aromatic hydrocarbons and polymerized unsaturated nitriles in a weight ratio of 70-80/30-20 therebetween.

11. The thermoplastic molding composition of Claim 9 wherein said small mode component contains a grafted phase, polymerized monovinylidene aromatic hydrocarbons and polymerized unsaturated nitriles in a weight ratio of 75-78/25-22 therebetween.

12. The thermoplastic molding composition of Claim 1 wherein said large mode component contains rubber at an amount of 14 to 20% relative to its weight.

13. The thermoplastic molding composition of Claim 12 wherein said large mode component contains a grafted phase, polymerized monovinylidene aromatic hydrocarbons and polymerized unsaturated nitriles in a weight ratio of 70-80/30-20 therebetween.

14. The thermoplastic molding composition of Claim 12 wherein said large mode component contains a grafted phase, polymerized monovinylidene aromatic hydrocarbons and polymerized unsaturated nitriles in a weight ratio of 75-78/25-22 therebetween.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 00/07616

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L69/00 C08L51/04 //(C08L69/00,51:04),(C08L51/04,69:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 535 124 A (BAYER AG) 13 August 1985 (1985-08-13) column 2, line 28 - line 44 examples claims 1-3,6,8	1-14
X	US 5 420 181 A (BAYER AG) 30 May 1995 (1995-05-30) examples; tables claims 1,2,6	1-14
X	US 4 880 875 A (BASF AG) 14 November 1989 (1989-11-14) abstract; examples; table 1 claim 1	1-14
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the 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 when the document is taken alone

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

"&" document member of the same patent family

Date of the actual completion of the international search
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INTERNATIONAL SEARCH REPORT

Int ional Application No
PCT/US 00/07616

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 677 162 A (MOBAY CORPORATION) 30 June 1987 (1987-06-30) cited in the application column 6, line 25 - line 29 examples claims 1-5,7,9	1-14
X	US 4 868 235 A (BASF AG) 19 September 1989 (1989-09-19) column 1, line 66 -column 2, line 4; examples claims 1-7	1-14
X	US 5 162 423 A (BASF AG) 10 November 1992 (1992-11-10) the whole document	1-14

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/US 00/07616

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		EP 0312929 A	26-04-1989
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		EP 0429957 A	05-06-1991

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权利要求书2页 说明书13页 附图页数0页

[54]发明名称 包含聚碳酸酯和接枝橡胶的具有改进低温韧性的组合物

[57]摘要

公开了一种热塑性模塑组合物，适用于制备具有改进性能的模塑制品，最特别的是其低温下的高韧性和高冲击强度。该组合物包括芳族聚碳酸酯和至少两种接枝橡胶的混合物的树脂共混物。接枝橡胶的混合物包括重均粒度小于0.3微米的“小型”组分和重均粒度等于或大于0.3微米的“大型”组分。

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权利要求书

1. 一种热塑性模塑组合物，其包含下述组分组成的共混物：

（i）60-80%聚碳酸酯树脂和

（ii）20-40%的至少两种接枝橡胶的混合物，

所述百分数基于共混物的重量，

其中，混合物包含：包含重均粒度小于0.3微米的接枝橡胶的小型组分，以及包含重均粒度至少为0.3微米的接枝橡胶的大型组分；该混合物另外的特征在于：存在于共混物中的所述小型组分和大型组分之间的重量比范围为3/27-7.5/22.5.

2. 权利要求1的热塑性模塑组合物，其中所述共混物含65-75%的聚碳酸酯和25-35%的所述混合物.

3. 权利要求1的热塑性模塑组合物，其中所述范围是3/27-5/25.

4. 权利要求1的热塑性模塑组合物，其中所述小型组分是乳液聚合的产物.

5. 权利要求1的热塑性模塑组合物，其中所述大型组分是本体聚合的产物.

6. 权利要求1的热塑性模塑组合物，其中所述大型组分是连续本体聚合的产物.

7. 权利要求1的热塑性模塑组合物，其中小型组分的重均粒度是0.15-0.28微米.

8. 权利要求1的热塑性模塑组合物，其中所述大型组分的重均粒度是0.35-0.65微米.

9. 权利要求1的热塑性模塑组合物，其中所述小型组分包含橡胶的量相对于该小型组分重量是50-60%.

10. 权利要求9的热塑性模塑组合物，其中所述小型组分包含接枝相，聚合的单亚乙烯基芳烃和聚合的不饱和腈之间的重量比为70-80/30-20.

11. 权利要求9的热塑性模塑组合物，其中所述小型组分包括接枝相，聚合的单亚乙烯基芳烃和聚合的不饱和腈之间的重量比为75-78/25-22.

12. 权利要求1的热塑性模塑组合物，其中所述大型组分包含橡

胶的量相对于该大型组分重量是 14~20%.

13. 权利要求 12 的热塑性模塑组合物，其中所述大型组分包括接枝相，聚合的单亚乙烯基芳烃和聚合的不饱和腈之间的重量比为 70-80/30-20.

14. 权利要求 12 的热塑性模塑组合物，其中所述大型组分包括接枝相，聚合的单亚乙烯基芳烃和聚合的不饱和腈之间的重量比为 75-78/25-22.

说 明 书

包含聚碳酸酯和接枝橡胶的具有改进低温韧性的组合物

发明领域

本发明涉及一种热塑性模塑组合物，并且特别涉及含聚碳酸酯和接枝橡胶的组合物.

发明概述

本发明公开了一种适于用作制备具有改进性能的模塑制品的热塑性模塑组合物，最特别的是具有高韧性和低温冲击强度. 该组合物包含芳族聚碳酸酯与至少两种接枝橡胶的混合物的树脂共混物. 接枝橡胶的混合物包含具有重均粒度小于 0.3 微米的“小型”组分（“small-mode”）和具有重均粒度等于或大于 0.3 微米的“大型”组分（“large-mode”）.

发明技术背景

已知热塑性模塑组合物含有接枝橡胶如 ABS 以及聚碳酸酯树脂. 以这种组合物为基础的商品，特别是 Bayer 公司出售的 Bayblend 组合物，长期以来得到了广泛的市场认可. 值得注意的是美国专利 3,954,905 和 4,560,725 已经公开了相关的组合物. 包括 ABS 组分的组合物也是周知的，ABS 的橡胶颗粒具有双峰粒度分布. 所述技术包括美国专利 3,509,237，该专利公开了一种组合物，该组合物含有第一类和第二类接枝共聚物，该组合物具有橡胶基体和一种单亚乙烯基芳烃与一种不饱和腈的共聚物覆盖物. 第一类和第二类接枝共聚物的数均粒径范围分别为 0.8-2.0 微米和 0.01-0.25 微米. 第一类接枝物被认为是悬浮聚合的产物，以及第二类接枝物是通过乳液聚合制备的. 值得注意的是美国专利 4,677,162 中已公开的组合物，它含有聚碳酸酯、接枝共聚物和冲击改性剂. 而接枝共聚物要求粒子平均粒径大于 0.75 微米，在应用实施例中要求的冲击改性剂包括一种具有与本发明相关化学组成和粒子大小的第二类接枝共聚物.

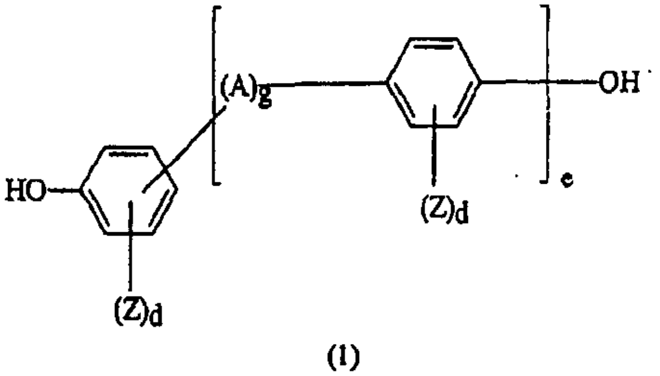
发明详述

本发明组合物包括含量约 60-80% 的聚碳酸酯树脂和含量为 20-40%至少两种接枝橡胶的混合物的树脂共混物. 在优选的实施方案中，共混物包含 65-75%的聚碳酸酯以及 25-35%的混合物，在所有的

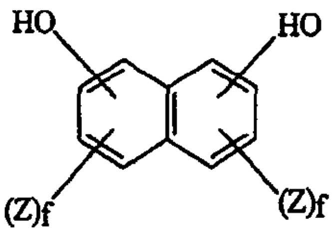
实例中，百分数均是相对于共混物重量的重量百分数．接枝橡胶混合物包含具有重均粒度小于 0.3 微米、优选约 0.15-0.28 微米的“小型”组分（ABS-s），以及“大型”组分（ABS-1），其中该组分的重均粒度至少为 0.3 微米，优选约 0.35-0.65 微米．混合物中 ABS-s 与 ABS-1 的重量比例范围为 3/27-7.5/22.5，优选 3/27-5/25．在优选的实施方案中，ABS-s 是众所周知的乳液聚合法的产物，以及 ABS-1 是已知的本体法、更优选连续本体聚合法的产物．

本发明范围内使用的芳族聚碳酸酯树脂包括均聚聚碳酸酯和共聚聚碳酸酯及其混合物．合适的聚碳酸酯其重均分子量为 10,000-200,000，优选 20,000-80,000，以及按 ASTM D-1238 方法，在 300℃下测得它们的熔体流动速率，为约 1-约 65g/10min，优选约 2-24g/10min．可以如下制备这些树脂，例如，用碳酸衍生物如碳酰氯和由缩聚法得到的二羟基化合物通过已知的两相界面法制备（参见德国 Offenlegungsschriften 2,063,050、2,063,052、1,570,703、2,211,956、2,211,957 和 2,248,817，法国专利 1,561,518，以及 H. Schnell 专论“《聚碳酸酯的化学与物理》（Chemistry and Physics of Polycarbonates）”，Interscience 出版社，纽约，1964 年，在此引入这些作为参考）．

在本发明内容中，适用于制备本发明人的聚碳酸酯的二羟基化合物，具有结构化学式（1）或（2）．



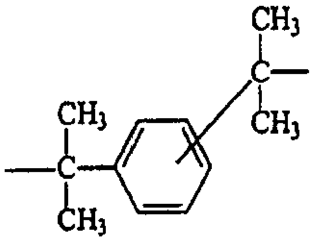
(1)



(2)

其中:

A表示1-8个碳原子的亚烷基（alkylene）、2-8个碳原子的亚烷基（alkylidene）、5-15个碳原子的亚环烷基（cycloalkylene）、5-15个碳原子的亚环烷基（cycloalkylidene）、羰基基团、氧原子、硫原子、－SO-、或者－SO_2-或者符合下式的基团:



e和g二者均表示数字0-1,

Z表示F、Cl、Br或者C_{1-4}烷基且如果在一个芳基基团中多个Z基团是取代基，则它们彼此可以相同或者不同;

d表示0-4的整数; 以及

f表示0-3的整数.

本发明实际应用中所用的二羟基化合物是: 氢醌、间苯二酚、双（羟苯基）烷烃类、双（羟苯基）醚类、双（羟苯基）酮类、双（羟苯基）亚砜类、双（羟苯基）硫醚类、双（羟苯基）砜类和α，α－双（羟苯基）二异丙苯类，以及它们的核烷基化化合物. 这些以及其它适用的芳族二羟基化合物描述在例如，美国专利5,126,428、5,104,723、5,041,521、5,034,457、3,028,356、2,999,835、3,148,172、2,991,273、3,271,367以及2,999,846中，在此引入这

些作为参考.

其它适用的双酚类例子包括：2,2-双（4-羟苯基）丙烷（双酚A）、2,4-双（4-羟苯基）-2-甲基丁烷、1,1-双（4-羟苯基）环己烷、α，α′-双（4-羟苯基）对二异丙苯、2,2-双（3-甲基-4-羟苯基）丙烷、2,2-双（3-氯代-4-羟苯基）丙烷、双（3,5-二甲基-4-羟苯基）甲烷、2,2-双（3,5-二甲基-4-羟苯基）丙烷、双（3,5-二甲基-4-羟苯基）硫醚、双（3,5-二甲基-4-羟苯基）亚砜、双（3,5-二甲基-4-羟苯基）砜、二羟基苯酮、2,4-双（3,5-二甲基-4-羟苯基）环己烷、α，α′-双（3,5-二甲基-4-羟苯基）对二异丙基苯以及4,4'-磺酰基联苯酚.

特别优选的芳族双酚的实例是2,2-双（4-羟苯基）丙烷、2,2-双（3,5-二甲基-4-羟苯基）丙烷和1,1-双（4-羟苯基）环己烷.

最优选的双酚是2,2-双（4-羟苯基）丙烷（双酚A）.

本发明的聚碳酸酯可以要求其结构单元衍生自一种或者多种合适的双酚类.

本发明实施中适合的树脂中包括了酚酞基聚碳酸酯、共聚碳酸酯类以及三聚碳酸酯类，如美国专利3,036,036和4,210,741中所描述，在此引用两个专利作为参考.

本发明中的聚碳酸酯也可以通过向其中缩聚少量如0.05-2.0mol%（相对于双酚而言）的多羟基化合物而被支化.

已经在很多专利中描述过这类聚碳酸酯，例如，德国Offenlegungsschriften 1,570,533、2,116,974和2,113,374；英国专利885,442和1,079,821；以及美国专利3,544,514. 下述是可以用于该目的的多羟基化合物的一些实例：间苯三酚、4,6-二甲基-2,4,6-三（4-羟苯基）庚烷、1,3,5-三（4-羟苯基）苯、1,1,1-三（4-羟苯基）乙烷、三（4-羟苯基）苯基甲烷、2,2-双（4,4-（4,4'-二羟基二苯基））环己基丙烷、2,4-双（4-羟基-1-异propylidine）酚、2,6-双（2'-二羟基5'-甲基苄基）-4-甲基酚、2,4-二羟基苯甲酸、2-（4-羟苯基）2-（2,4-二羟苯基）丙烷和1,4-双（4,4'-二羟基三苯基甲基）苯. 其它一些多官能团化合物是：2,4-二羟基苯甲酸、1,3,5-苯三酸、氰尿酰氯和3,3-双（4-羟苯基）2-氧代-2,3-二氢吲哚.

除了上面已经提及的缩聚法以外，用于制备本发明聚碳酸酯类的其它方法有均相缩聚法和酯基转移法。合适的方法公开在美国专利3,028,365、2,999,846、3,153,008和2,991,273中，在此引用作为参考。

制备聚碳酸酯的优选方法是界面缩聚法。

可以用其它类合成方法制备本发明聚碳酸酯，如美国专利3,912,688公开的方法，在此引用作为参考。

商业可购买到合适的聚碳酸酯树脂，例如 Makrolon 2400、Makrolon2600、Makrolon2800 和 Makrolon3100，所有这些都是双酚基均聚聚碳酸酯树脂，只是各自分子量不同而有区别，它们的特征在于：按照 ASTM D-1238 测定它们的熔体流动指数（MFR）分别是约16.5-24、13-16、7.5-13.0和3.5-6.5g/10min。这些产品都是宾夕法尼亚州匹兹堡的 Bayer 公司的产品。

适合本发明实际应用的聚碳酸酯树脂是已知的，且它们的结构和制备方法已经公开在例如美国专利3,030,331、3,169,121、3,395,119、3,729,447、4,255,556、4,260,731、4,369,303和4,714,746中，在此引入作为参考。

包含在本发明组合物中的混合物含有其重均粒度小于0.3微米、优选0.15-0.28微米的“小型”组分（ABS-s），以及其重均粒度至少为0.3微米、优选0.35-0.65微米的“大型”组分（ABS-l）。混合物中 ABS-s 与 ABS-l 的重量比范围为3/27-7.5/22.5，优选3/27-5/25。

在速混物（instant mixture）中两种接枝橡胶组分的接枝相包含单亚乙烯基芳烃和不饱和腈。这类单体包括至少50.0wt%、优选至少75wt%的接枝相。最希望的是，这类单体包括至少90wt%的接枝相。可以包括少量、优选小于10%的其它共单体。在制备接枝相中可使用的单亚乙烯基芳烃实例包括苯乙烯，α－烷基单亚乙烯基单芳族化合物如α－甲基苯乙烯、α－乙基苯乙烯、α－甲基－乙烯基甲苯、α－甲基二烷基苯乙烯等，环上被取代的烷基苯乙烯类如乙烯基甲苯、邻－乙基苯乙烯、对－乙基苯乙烯、2,4-二甲基苯乙烯等，环上被取代的卤代苯乙烯例如邻－氯代苯乙烯、对－氯代苯乙烯、邻－溴代苯乙烯、2,4-二氯代苯乙烯等，环上被烷基取代、环上被卤代的苯乙烯

类如 2-氯代－4-甲基苯乙烯、2,6-二氯代－4-甲基苯乙烯等，乙烯基萘、乙烯基蒽等．烷基取代基通常含有 1-4 个碳原子且可以包括异丙基和异丁基．如果需要，可以采用这种单亚乙烯基芳族单体的混合物．

用于制备接枝相的不饱和腈类的实例，包括丙烯腈、甲基丙烯腈和乙基丙烯腈，这些腈类可以单独使用或者与其它腈类混合使用．

在接枝相中可以共聚少量的其它单体的实例包括：共轭 1,3-二烯例如丁二烯、异戊二烯等，α－或β－不饱和一元酸及其衍生物例如丙烯酸、丙烯酸甲酯、丙烯酸乙酯、丙烯酸丁酯、丙烯酸-2-乙基己酯、甲基丙烯酸及其相应的酯类，丙烯酰胺、甲基丙烯酰胺，乙烯基卤代物如氯乙烯、乙烯基溴等，1,1-氯乙烯、1,1-溴乙烯等，乙烯基酯类如乙酸乙烯酯、丙酸乙烯酯等，马来酸二烷基酯类或富马酸二烷基酯类如马来酸二甲酯、马来酸二乙酯、马来酸二丁酯、相对应的富马酸酯类等．

形成接枝相的可聚合单体混合物含有至少 20wt%的单亚乙烯基芳族单体，且优选至少 50wt%的单亚乙烯基芳族单体．它们也可以包含至少 5wt%的不饱和腈和优选至少 10wt%的不饱和腈．从非常有利于商业实用价值的角度看，单体配方中含有 20-95wt%、且优选 60-85wt%的亚乙烯基芳烃，和 80-5wt%、且优选 40-15wt%不饱和腈．

在两种接枝橡胶组分中的橡胶基体是二烯橡胶，所述橡胶基体在聚合过程中以及在其存在下接枝相被接枝到其上．它们是由一种或多种共轭 1,3-二烯类如丁二烯、异戊二烯、戊间二烯、氯丁二烯等制备的．这类橡胶包括共轭 1,3-二烯与多至等重量的一种或多种可共聚的单烯属不饱和单体的均聚物和共聚体，其中单烯属不饱和单体例如单亚乙烯基芳烃（例如苯乙烯；芳烷基－苯乙烯如邻－、间－和对－甲基苯乙烯，2,4-二甲基苯乙烯，芳－乙基苯乙烯、对叔丁基苯乙烯等；α－烷基苯乙烯如α－甲基苯乙烯、α－乙基苯乙烯、α－甲基－对乙基苯乙烯等；乙烯基萘等），芳卤代单亚乙烯基芳烃类（例如邻－、间－和对－氯代苯乙烯，2,4-二溴代苯乙烯，2-甲基－4-氯代苯乙烯等），丙烯腈，甲基丙烯腈，丙烯酸烷基酯类（例如丙烯酸甲酯、丙烯酸丁酯、丙烯酸-2-乙基己酯等），相对应的甲基丙烯酸烷基酯，丙烯酰胺类（例如丙烯酰胺、甲基丙烯酰胺、N-丁基丙烯

酰胺等），不饱和酮类（例如乙烯基甲基酮、甲基异丙基酮等），α－烯烃类（例如乙烯、丙烯等），吡啶，乙烯基酯类（例如醋酸乙烯酯、硬脂酸乙烯酯等），乙烯基和亚乙烯基卤化物（例如乙烯基和亚乙烯基的氯化物和溴化物等）等等。

相对于形成橡胶的单体重量而言，可以通过向可聚合的混合物中加入最高用量达到约 2%的常规交联剂而使橡胶基体发生交联，交联剂为例如二乙烯基苯、马来酸二烯丙基酯、富马酸二烯丙基酯、己二酸二烯丙基酯、丙烯酸烯丙基酯、甲基丙烯酸烯丙基酯、多元醇的二丙烯酸酯类和二甲基丙烯酸酯类，如二甲基丙烯酸乙二醇酯。

优选的橡胶类是基本由 75wt%－100wt%丁二烯和/或异戊二烯及最高含量达 25wt%的下述单体组成的那些橡胶，这些单体选自单亚乙烯基芳烃（例如苯乙烯）和不饱和腈（例如丙烯腈），或它们的混合物，特别有利的基体是丁二烯均聚物或 90-95wt%的丁二烯以及 5-10wt%的丙烯腈或苯乙烯的共聚物。

优选地，本发明的 ABS-s 组分是用已知的乳液聚合法制备的。相对于 ABS-s 组分的重量而言，它的橡胶基体的量可达到约 50-60%，且接枝相的特征在于聚合的单亚乙烯基芳烃和聚合的不饱和腈的重量比为 70-80/30-20，优选 75-78/25-22。

在乳液聚合法中，通过使用合适的乳化剂将单体和橡胶基体在水中进行乳化，合适的乳化剂例如有脂肪酸皂类、高分子量烷基或烷芳基硫酸盐和磺酸盐的碱金属或铵皂类、长链脂肪族胺类的无机酸盐类等。已证明特别有利的乳化剂是油酸钠、棕榈酸钠、硬脂酸钠以及其它的钠皂类。通常地，提供的乳化剂用量是每 100 重量份数的单体中加入乳化剂用量约 1-15 重量份数。提供的水用量是每份单体中加入水约 1-4 份，如果需要更大地稀释液时甚至可进一步加大这个比例。

如果需要，在橡胶基体的乳液聚合中形成的水胶乳可提供水介质，在有或者没有另外加入的乳化剂的情况下，加入单体到其中。但是，橡胶可以溶解在单体和乳化的混合物中，或者可以单独制备其胶乳。

一般将各种水溶性自由基聚合引发剂用于橡胶单体乳液聚合中，其包括常用的过氧化物和 perazo 催化剂，并且所得的胶乳可以用作水介质，与共聚物单体进行掺和。在这种方法中，用于橡胶聚合

的催化剂可以全部或部分用作用于接枝聚合的催化剂。然而，可以在接枝聚合时加入另外的催化剂 。适用的过氧化物催化剂的典型实例有：碱金属的过氧化物、过硫酸盐、过硼酸盐、过乙酸盐和过碳酸盐类，以及过氧化氢。如果需要，可以将催化剂活化形成氧化还原体系。此外，如果包括一种油溶性催化剂例如上文指明的适用于本体乳液聚合法中的那些催化剂将是有利的。然而，仍可以采用其它产生自由基的催化剂如光化辐射作用。

需要时可包括链转移剂和其它聚合改性剂，且通常加入较高级烷基硫醇是有利的，例如叔十二烷基硫醇，既可以作为助催化剂也可以作为调节剂。此外，可以加入抗氧剂和稳定剂如烷基化的酚类。

然后在 20-100℃、搅拌并用惰性气体保护下，聚合乳液混合物。采用的压力是每平方英寸 1-100 磅，以及可以在反应周期的某一阶段递增地或者连续地加入单体和/或另外的催化剂。 聚合反应持续进行到基本全部即 90%以上的单体反应完成为止。然后将剩余单体和其它挥发性组分从胶乳中蒸馏出来，随后脱水并进行干燥。

本发明组合物中的 ASB-1 组分优选用已知的本体法制备，更优选连续本体聚合法制备。在这种接枝共聚物中的橡胶优选是丁二烯或者丁二烯/苯乙烯共聚物（重量比 90/10）以及相对于接枝共聚物的重量而言橡胶含量约为 14-20%。接枝相的特征在于已聚合的单亚乙烯基芳烃与已聚合的不饱和腈的重量比是 73-80/27-20，优选 75-78/25-22。

在连续本体聚合法中，先将橡胶基体溶于单体和溶液中，再将引发剂和其它一些任选的组分如溶剂连续加入到搅拌或者不搅拌的反应器中，得到含基本全部均一组成的聚合混合物的连续聚合反应区域。可以采用多个串联反应器，以达到要求的转化率，在每个反应器中以连续方式进行聚合反应。当聚合反应进行到所要求的转化率水平后，将剩余单体从聚合物中汽提出来。无论采用的是一个聚合反应器还是一系列聚合反应器，脱挥发分的过程都是相同的，通常是在分离装置如刮板式薄膜脱挥发分装置或沉降单纱脱挥发分装置（falling strand devolatilizer）中进行。

采用本体聚合法连续生产接枝橡胶的常用现有技术方法见述于美国专利 3,243,481、3,337,750、3,511,895 以及 4,417,030，后者

的内容在此引用作为参考。

聚合反应可以通过任何自由基发生引发剂引发，该引发剂可以促进接枝并可在设计的反应温度下被活化。适用的引发剂包括常规的单体可溶解的过氧化物和 perazo 化合物。典型的引发剂有：叔丁基过氧化新癸酸酯、叔丁基过氧化－2－乙基己酸酯、1-叔丁基偶氮－1-氰基环己烷、过氧化二叔丁基、过氧化苯甲酰基、过氧化月桂酰、过氧化油基、过氧化甲苯酰、二过邻苯二甲酸二叔丁基酯、过乙酸叔丁基酯、过苯甲酸叔丁基酯、过氧化二枯基、叔丁基过氧化异丙基碳酸酯、2,5-二甲基－2,5-二（叔丁基过氧基）己烷、2,5-二甲基－2,5-二（叔丁基过氧基）己炔－3、过氧化氢叔丁基、bumene 过氧化氢、对甲烷过氧化氢、环戊烷、过氧化氢、过氧化氢二异丙基苯、对叔丁基枯烯过氧化氢、penant 过氧化氢、2,5-二甲基己烷化-2,5-二过氧化氢，以及过碳酸盐化合物如叔丁基－2-乙基己基单过氧碳酸盐等，及它们的混合物。

根据单体及所需要的聚合周期，通常加入的引发剂量为可聚合物质重量的 0.001-1.0wt%，且优选约 0.005-0.5wt%。

经常需要加入分子量调节剂如硫醇、卤化物和萜，加入量相当少，占可聚合物质重量的约 0.001-1.0wt%。此外，还可视需要而加入小量的抗氧剂或稳定剂如常规烷基化酚类。另一方面，这些物质可以在聚合过程中也可以在聚合后加入。配制剂中也可以包含其他添加剂如增塑剂、润滑剂、着色剂和适用的或者可分散在其中的非反应性预制聚合物物质。

溶剂或稀释剂可用于稀释反应混合物以达到以下稀释程度：搅拌反应器中搅拌所需要的功率不过量。部分或者全部的这些稀释剂或者作为添加的组分可与橡胶在单体中的溶液一起加入，或者将所用橡胶先溶解在适用溶剂中后再与稀释剂一起加入。稀释剂也可以独立地加入到一个或多个反应器中。

稀释剂可以是含 6-10 个碳原子的液体芳烃，例如苯、甲苯、二甲苯、乙基苯、对异丙基苯甲烷、枯烯或它们的混合物。其他有机溶剂如饱和脂肪烃例如己烷、环己烷、环戊烷或者含 5-7 个碳原子的其它脂肪烃，也可以使用酮类如丁酮、甲基环戊烷、甲基·异丁基酮、环己烷或甲基·丙基酮。优选丁酮。

单独制备未接枝基体共聚物的优选连续本体法见美国专利3,813,369所公开内容，在此引入作为参考．总之，单体被连续地加入到已混合好的包含液相和气相的聚合反应区中．液相含有作为溶剂的单体组合物，由单体组合物形成的共聚物被溶解在其中．液相上面的气相包括单体组合物．液体和气体连续地从反应区中取出，并以约等于单体聚合和排出的速度进行补料．取出的气相可以通过回流冷凝作用被冷凝，作为加入到反应区的单体组合物中一部分返回到反应区中．取出的聚合物和单体的混合物通过上述类型的一个或多个脱挥发分装置，将聚合物分离出来．然后将热熔体用常规设备造粒，而分离出来的单体被冷凝和返回到反应区．链转移剂和液体溶剂、引发剂、和上面所述与连续本体接枝聚合法相关的其他添加剂可以与单体组合物一起或者单独地连续加入到反应区中．

橡胶接枝共聚物即橡胶基体及其接枝共聚物上层物（superstrate）的平均粒度，是根据每种橡胶接枝共聚物组分中几种粒径的粒子得到的平均值，粒度是用光学沉降仪测定的，具体方法按照 Graves. M. J 等的 British Chemical Engineering（英国化学工程）（1964年）、卷9第742-744页中所发表的“离心光学沉降仪亚筛粉末粒径分析”法．替换地，可以使用电子显微镜法．

本发明组合物可以用本技术领域专业人员所熟知的传统方法和下述步骤进行制备和加工．

实施例

制备说明本发明的组合物且其性能已被测定，下表概述了测定的结果．在制备组合物中，使用了下述组分：

聚碳酸酯：以双酚A为基础的均聚聚碳酸酯，根据 ASTM D-1238，测定熔体流动速率约11g/10min.

ABS-1(a)：接枝共聚物，含16%丁二烯/苯乙烯（90/10wt%）橡胶，并且具有S/AN比等于77/23，重均粒度0.64微米．

ABS-1(b)：接枝共聚物，含16%丁二烯/苯乙烯（90/10wt%）橡胶，并且具有S/AN比等于77/23，重均粒度0.35微米．

ABS-s：接枝共聚物，含53%丁二烯橡胶，具有SAN比等于73/27，重均粒度0.28微米．

SAN：共聚物相，苯乙烯/丙烯腈比＝72.5/27.5.

维卡温度由ASTM1525测定，伊佐德冲击强度根据ASTM D256测定，多轴冲击强度根据ASTM D3763（测试速度6.7m/s选择的冲击物质在冲击过程中能使速度损失最小）测定，韧性：下表中给出的实例的韧性破坏的定义依据是“通用汽车工程标准”GMP. ABS+PC.002.使用多轴冲击试验时，如果在测试样品打孔时，裂纹辐射到距离冲击点中心不超过10mm，则测试样品认为呈现韧性破坏。报告的韧性破坏表示以这种方式韧性破坏的样品百分数，以15个测试样品为基础计。

组合物中也包括了常规数量的脱模剂和抗氧剂，本发明内容中它们不是关键的。本发明中组合物（实施例1、2、3和4中所示）与对应的组合物实施例5进行了比较，虽然实施例5含有相应量的橡胶，具有等同的或更好的维卡性能和伊佐德冲击强度，但其特点是在低温下比本发明组合物更脆。

	1	2	3	4	5（比较）
聚碳酸酯	70	70	70	70	70
ABS-I(a)	30	27			
ABS-I(b)			30	27	
ABS-s		3		3	13
SAN					17
橡胶总量	4.8	5.91	4.8	5.91	6.89
性能					
维卡温度 (°C) 1Kg@120°C/hr	144	144.9	144.2	144.3	145
冲击强度，伊佐德 (ft-lb/in)					
1/8" 23°C	11.7	10.9	10.9	11	11.5
1/8" -30°C	5.3	7.1	5.7	7.8	9
多轴冲击强度，在 -30°C (J)					
(E最大)	50	56	52	51	46
(E破坏)	55	60	56	56	48
脆性/韧性	9/6	1/14	10/5	2/13	10/0
韧性破坏，%	40	93	33	87	0

虽然为达到说明的目的，前面已经详细地描述了本发明，但是应该理解为完全是为了该目的，除去受本发明的权利要求的限定以外，在不背离本发明宗旨和范围的条件下，本领域专业人员可能作些改变，这些也是本发明范围．