

SILICONE-ACRYLATE IMPACT MODIFIER

BACKGROUND

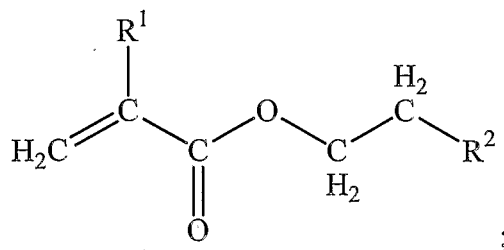
The disclosure relates generally to silicone-acrylate rubber compositions and their use as impact modifiers in resin molding compositions, particularly those comprising thermoplastic resins. Furthermore, the disclosure also relates to an emulsion polymerization method for making the silicone-acrylate impact modifiers. As used hereinafter, the expressions "silicone-acrylate rubber" and "silicone-acrylate rubber graft hybrid" mean an interpenetrating composite of silicone rubber and polyacrylate rubber, where the silicone rubber and polyacrylate rubber are entangled in an inseparable fashion at the molecular level.

Butadiene-based impact modifiers, such as acrylonitrile-butadiene-styrene (also called ABS) copolymers and methyl methacrylate-butadiene-styrene (also called MBS) copolymers have been previously used to improve the impact performance of thermoplastic materials. However, due to the presence of unsaturation, these butadiene-based copolymers respond poorly to weathering. Weathering is a phenomenon where the combined effect of several natural elements, particularly oxygen in air and sunlight act upon the polymer thereby causing the material to degrade. Generally, this degradation is observable by a yellowing and loss of surface gloss of the polymer material. Impact modifiers based on acrylonitrile-styrene-acrylate (also called ASA) copolymers avoid the issues faced by the butadiene-based polymers, however, these materials only have room temperature ductility. Acrylate rubbers are widely used for impact modification of thermoplastic materials where weathering is a concern. However, the impact strength of acrylate rubber-modified thermoplastic materials at low temperatures, such as 0 °C, or below are substantially reduced, as compared to thermoplastic materials containing other organic blends, such as the butadiene-based polymers. Efforts have been made to use silicone-based materials to improve low temperature impact. For example, silicone-polycarbonate copolymers show good ductility at -40 °C, but they can be used only in polycarbonates and polycarbonate blends. Efforts to improve the low temperature impact of thermoplastic polymer compositions by using silicone rubber-based impact modifiers,

such as Mitsubishi Rayon's S 2001 are known. However, the low temperature impact and ductility performance, as measured for example, by the ductile-to-brittle transition temperature (hereinafter referred to as "DBTT") is in some cases not up to the desired mark. Therefore, there is a continued need for impact modifiers that can afford superior impact properties, lower ductile-to-brittle transition temperatures (hereinafter sometimes referred to as DBTT's), and outstanding weatherability performance, that is, slow down or prevent yellowing and loss of surface gloss, in polymer compositions and articles comprising these polymer compositions. Such impact modifiers, when incorporated into polymer resin systems are expected to find a wide variety of applications, especially outdoor applications.

BRIEF DESCRIPTION

Briefly, one embodiment of the disclosure is a silicone-acrylate impact modifier composition, where the impact modifier composition comprises structural units derived from: at least one silicone rubber monomer, a branched acrylate rubber monomer having the formula:

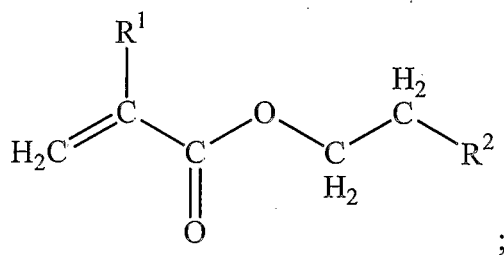


where R^1 is selected from hydrogen and $\text{C}_1 - \text{C}_8$ linear and branched hydrocarbyl groups; and R^2 is a branched $\text{C}_3 - \text{C}_{16}$ hydrocarbyl group; a first graft link monomer, a polymerizable alkenyl-containing organic material, and a second graft link monomer.

Another embodiment of the disclosure is a silicone-acrylate impact modifier composition, where the impact modifier composition comprises structural units derived from: a silicone rubber monomer comprising octamethylcyclotetrasiloxane and tetraethoxysilane; a branched acrylate rubber monomer selected from the group consisting of iso-octyl acrylate, 6-methyloctyl, 7-methyloctyl, and combinations of the foregoing branched acrylate rubber monomers; at least one first graft link monomer

selected from the group consisting of (gamma-methacryloxypropyl)(dimethoxy)methylsilane and (3-mercaptopropyl)trimethoxysilane; a polymerizable alkenyl-containing organic material comprising at least one of styrene, alpha-methylstyrene, acrylonitrile, methacrylonitrile, methyl methacrylate; and at least one second graft link monomer selected from the group consisting of allyl methacrylate, triallyl cyanurate, and triallyl isocyanurate.

Another embodiment of the disclosure is a molding composition comprising a polymer resin and a silicone-acrylate impact modifier composition, wherein said impact modifier composition comprises structural units derived from: at least one silicone rubber monomer, a branched acrylate rubber monomer having the formula:

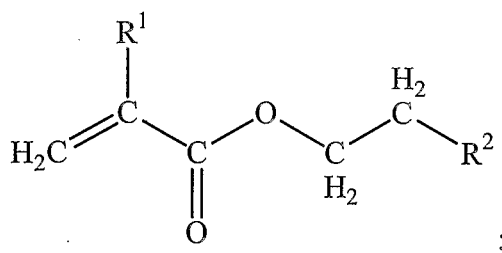


wherein R^1 is selected from hydrogen and $\text{C}_1 - \text{C}_8$ linear and branched hydrocarbyl groups; and R^2 is a branched $\text{C}_3 - \text{C}_{16}$ hydrocarbyl group; a first graft link monomer, a polymerizable alkenyl-containing organic material, and a second graft link monomer; wherein said molding composition has a ductile-to-brittle transition temperature from about 0°C to about -60°C .

Another embodiment of the disclosure is a molding composition comprising a polymer resin and a silicone-acrylate impact modifier composition, wherein the silicone-acrylate impact modifier composition comprises structural units derived from: a silicone rubber monomer comprising octamethylcyclotetrasiloxane and tetraethoxysilane; a branched acrylate rubber monomer selected from the group consisting of iso-octyl acrylate, 6-methyloctyl, 7-methyloctyl, and combinations of the foregoing branched acrylate rubber monomers; at least one first graft link monomer selected from the group consisting of (gamma-methacryloxypropyl)(dimethoxy)methylsilane and (3-

mercaptopropyl)trimethoxysilane; a polymerizable alkenyl-containing organic material comprising at least one of styrene, alpha-methylstyrene, acrylonitrile, methacrylonitrile, methyl methacrylate; and at least one second graft link monomer selected from the group consisting of allyl methacrylate and triallyl cyanurate; wherein said molding composition has a ductile-to-brittle transition temperature of less than or equal to about -60°C .

Another embodiment of the disclosure is a method for making a silicone-acrylate impact modifier composition, where the method comprises: emulsion polymerizing at least one silicone rubber monomer and a first graft link monomer at a temperature from about 30°C to about 110°C to form a silicone rubber latex; adding to said silicone rubber latex, at a pH of about 4 to about 9.5, and a temperature of about 20°C to about 90°C , at least one branched acrylate rubber monomer to provide a latex comprising an emulsion polymerized silicone-acrylate rubber hybrid; grafting said silicone-acrylate rubber hybrid with a polymerizable alkenyl containing organic material and a second graft link monomer to form a graft silicone-acrylate rubber hybrid latex; and coagulating, washing, and drying said graft silicone-acrylate rubber hybrid latex to provide said silicone rubber impact modifier composition; wherein said at least one branched acrylate rubber monomer has the formula:



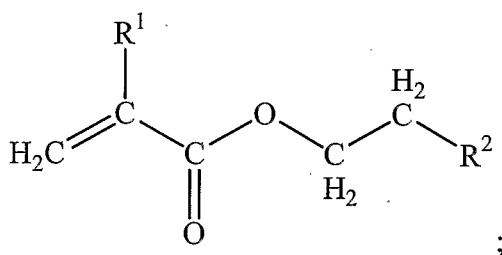
wherein R^1 is selected from H and $\text{C}_1 - \text{C}_8$ linear and branched hydrocarbyl groups; and R^2 is a branched $\text{C}_3 - \text{C}_{16}$ hydrocarbyl group.

DETAILED DESCRIPTION

The impact modifier compositions disclosed herein display many of the properties that makes them valuable materials for use in outdoor applications, especially in cold climates. The impact modifier compositions display ductile-to-brittle transition

temperatures (hereinafter sometimes referred to as "DBTT") lower than or equal to about -40°C , outstanding low temperature ductility and impact, and excellent weatherability performance, while retaining the other desirable properties, such as heat distortion temperature (hereinafter sometimes referred to as "HDT"), tensile and flexural modulus, and melt volume ratio (hereinafter sometimes referred to as "MVR").

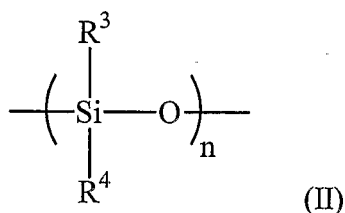
Suitable branched acrylates useful for the silicone-acrylate impact modifier compositions of the disclosure are represented by formula (I):



where R^1 is selected from hydrogen and $\text{C}_1 - \text{C}_8$ linear and branched hydrocarbyl groups; and R^2 is a branched $\text{C}_3 - \text{C}_{16}$ hydrocarbyl group. In an embodiment, the branched acrylate is one where R^1 is hydrogen and R^2 is at least one branched hydrocarbyl radical selected from 4-methylpentyl, 4-methylhexyl, and 5-methylhexyl. In general the branched acrylates of formula (I) have structures in which the R^2 group is separated from the acrylate acyl oxygen (that is, the oxygen atom located next to the acrylate carbonyl group) by at least 2 CH_2 groups. In a particular embodiment, the branched acrylate is 6-methylheptyl acrylate. The branched acrylates can be prepared by methods known in the art. For example, reaction of acryloyl chloride with the appropriate branched alcohol in the presence of a tertiary amine scavenger to trap the hydrogen chloride by-product furnishes the desired branched acrylate ester. Some of the branched acrylates, such as 6-methylheptyl acrylate are commercially available from vendors, such as Aldrich Chemical Company. In another embodiment, the silicone-acrylate impact modifier composition further comprises structural units derived from at least one acrylate monomer selected from the group consisting of methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate.

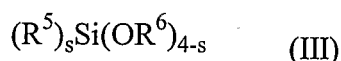
The silicone-acrylate impact modifier comprises structural units derived from silicone rubber monomers. A variety of silicone rubber monomers can be used. In general, the silicone rubber monomer comprises at least one of a cyclic siloxane, tetraalkoxysilane, trialkoxysilane, (acryloxy)alkoxysilane, (mercaptoalkyl)alkoxysilane, vinylalkoxysilane, and allylalkoxysilane.

The silicone rubber monomer comprises at least one of a cyclic siloxane of the formula (II):



where R^3 and R^4 are independently selected from hydrogen and $\text{C}_1 - \text{C}_{10}$ alkyl and aryl radicals; and "n" is an integer having a value from about 3 to about 20. In some embodiments, R^3 or R^4 , or both can be aryl groups. Suitable non-limiting examples of aryl radicals include phenyl, tolyl, xylyl, and the like. Phenyl radical is a preferred aryl radical since the phenyl-substituted silicone rubber monomers are relatively more readily available. Some of the preferred silicone rubber monomers include cyclic siloxanes, such as octamethylcyclotetrasiloxane, as shown for example in the Encyclopedia of Polymer Science and Engineering, volume 15, 2nd Edition, pp. 205-308 (1989), John Wiley and Sons. Other examples of cyclic siloxanes include without limitation, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, trimethyltriphenylcyclotrisiloxane, tetramethyltetraphenylcyclotetrasiloxane, tetramethyltetravinylcyclotetrasiloxane and octaphenylcyclotetrasiloxane. These or similar cyclic siloxanes may be used alone or in combination.

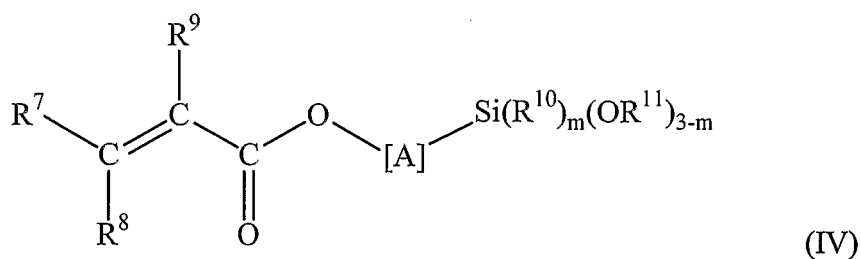
The tetraalkoxysilane and trialkoxysilane type silicone rubber monomers are represented by the general formula (III):



where R^5 independently comprises hydrogen and $C_1 - C_{10}$ alkyl and aryl radicals; R^6 independently comprises $C_1 - C_4$ hydrocarbyl radicals; and "s" is an integer having a value from about 0 to about 1. One or more of the hydrocarbyl radicals in the tetraalkoxysilane can also be aryl radicals. Suitable non-limiting examples of aryl radicals include phenyl, tolyl, xylyl, and the like. Phenyl radical is a preferred aryl radical since the phenyl-substituted silicone rubber monomers are relatively more readily available. In an embodiment, (hydrocarbyl)trialkoxysilanes can also be as suitable silicone rubber monomers. Examples of suitable tetraalkoxysilanes include, but are not intended to be limited to tetramethoxysilane, tetraethoxysilane, tetraisopropoxysilane, and tetrabutyloxysilane, and the like. Examples of suitable (hydrocarbyl)trialkoxysilanes include, but are not intended to be limited to methyltrimethoxysilane, methyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, and the like. In a particular embodiment, tetraethoxysilane or tetraethylorthosilicate (hereinafter sometimes also referred to as "TEOS") can be conveniently used as a silicone rubber monomer. The tetraalkoxysilanes and trialkoxysilanes can be used at from about 0.1% to about 30% by weight of the overall monomer mixture used for preparing the silicone-acrylate impact modifier composition.

The first graft link monomer used for preparing the silicone rubber impact modifier composition comprises at least one of an (acryloxy)alkoxysilane, a (mercaptoalkyl)alkoxysilane, a vinylalkoxysilane, and an allylalkoxysilane.

Suitable (acryloxyalkyl)silanes that can be used as the first graft link monomer are of the formula (IV):

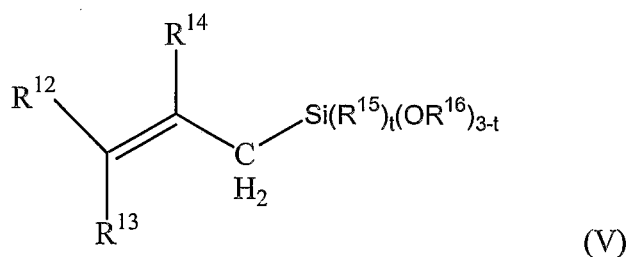


where R^7 , R^8 , and R^9 are independently selected from hydrogen and $C_1 - C_6$ hydrocarbyl radicals; [A] is a $C_1 - C_{12}$ alkylene radical; R^{10} is selected from hydrogen

and $C_1 - C_{10}$ hydrocarbyl radicals; R^{11} is selected from $C_1 - C_6$ hydrocarbyl radicals; and "m" is integer having a value from 0 to about 1. In an embodiment, R^7 and R^8 are hydrogen, R^9 is methyl, and [A] is a $-\text{CH}_2\text{CH}_2\text{CH}_2-$ radical. In another embodiment, (gamma-methacryloxypropyl)silanes, in which R^{10} is a methyl or a phenyl group; and R^{11} is a methyl, ethyl, or an isopropyl group can be used in the impact modifier compositions disclosed herein. (Gamma-methacryloxypropyl)dimethoxymethylsilane and (Gamma-methacryloxypropyl)trimethoxysilane are particularly convenient and versatile first graft link monomers due to their ready availability. The (acryloxy)silanes can be used at from about 0.1% to about 30% by weight of the overall monomer mixture used for preparing the silicone-acrylate impact modifier composition.

Mercaptan-functionalized (hydrocarbyl)trialkoxysilanes are particularly valuable silicone rubber monomers. Examples of suitable mercaptan-functionalized (hydrocarbyl)trialkoxysilanes include (3-mercaptopropyl)trimethoxysilane (hereinafter sometimes referred to as "MPTMS"), (4-mercaptobutyl)trimethoxysilane, (3-mercaptoethyl)trimethoxysilane, (3-mercaptopropyl)triethoxysilane, and the like.

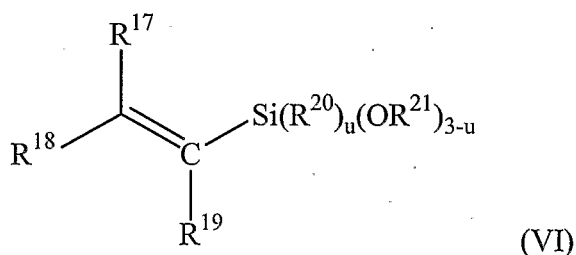
Another type of possible silicone rubber monomer is a substituted or an unsubstituted allylalkoxysilane of the formula (V):



where R^{12} , R^{13} , and R^{14} are independently selected from hydrogen and $C_1 - C_4$ hydrocarbyl radicals; R^{15} independently comprises $C_1 - C_8$ hydrocarbyl radicals, R^{16} independently comprises $C_1 - C_4$ hydrocarbyl radicals, and "t" is an integer having a value from 0 to about 1. Examples of suitable allylalkoxysilanes include, but are not intended to be limited to allyltrimethoxysilane, allyltriethoxysilane, crotyltrimethoxysilane, crotyltriethoxysilane, (3-phenyl-2-propenyl)trimethoxysilane, and the like. In a particular embodiment, allyltrimethoxysilane is a suitable silicone

rubber monomer. In other embodiments, the silicone rubber monomer can also comprise compounds that have 2 alkoxy groups and 2 allylic groups about the silicon atom. Furthermore, the 2 alkoxy groups can be the same or different. Likewise, the 2 allylic groups can be the same or different. The allylalkoxysilanes can be used at from about 0.1% to about 30% by weight of the overall monomer mixture used for preparing the silicone-acrylate impact modifier composition.

Vinylalkoxysilanes can also be used as suitable first graft link monomers. Suitable vinylalkoxysilanes have the formula (VI):



where R^{17} , R^{18} , and R^{19} are independently selected from hydrogen and $\text{C}_1 - \text{C}_4$ hydrocarbyl radicals; R^{20} independently comprises $\text{C}_1 - \text{C}_8$ hydrocarbyl radicals, R^{21} independently comprises $\text{C}_1 - \text{C}_4$ hydrocarbyl radicals, and "u" is an integer having a value from 0 to about 1. Suitable vinylalkoxysilanes include vinyltrimethoxysilane, vinyltriethoxysilane, (1-propenyl)trimethoxysilane, styryltrimethoxysilane, divinyl dimethoxysilane, divinyl diethoxysilane, and the like. The vinylalkoxysilanes can be used at from about 0.1% to about 30% by weight of the overall monomer mixture used for preparing the silicone-acrylate impact modifier composition.

In an embodiment, the first graft link monomer is at least one selected from the group consisting of (gamma-methacryloxypropyl)(dimethoxy)methylsilane, (3-mercaptopropyl)trimethoxysilane, vinyltrimethoxysilane, and allyltrimethoxysilane. It will be apparent to those skilled in the art that different combinations of the above-mentioned different types of first graft link monomer can be used to form the silicone-acrylate impact modifier composition.

The second graft link monomer is at least one polyethylenically unsaturated compound having at least one allyl group. In one embodiment, the polyethylenically

unsaturated compound is at least one selected from the group consisting of allyl methacrylate, triallyl cyanurate (hereinafter sometimes referred to as "TAC"), triallyl isocyanurate, and diallylmaleate.

The polymerizable alkenyl containing organic material comprises at least one vinyl aromatic monomer, olefinic nitrile; and branched and unbranched acrylate monomers. Suitable alkenyl containing organic materials used for preparing the silicone rubber compositions includes without limitation: styrene, divinylbenzene, alpha-methylstyrene, vinyl toluene, halogenated styrene, and the like; methacrylates, such as methyl methacrylate and 2-ethylhexyl methacrylate; linear acrylates such as methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate; n-pentyl acrylate, n-hexyl acrylate, n-heptyl acrylate, and n-octyl acrylate; olefinic nitriles, such as acrylonitrile and methacrylonitrile; olefins such as ethylene, propylene, butadiene, isoprene, and chloroprene; chloroprene, and 5-vinyl-2-norbornene, and other vinyl compounds such as acrylamides, N-(mono- or di-substituted alkyl)acrylamides, vinylimidazole, vinyl acetate, vinyl alkyl ethers, vinyl chloride, vinyl furan, N-vinyl carbazole, vinyl pyridine, vinyl pyrrolidines, vinyl acetate, vinyl chloride, vinyl alkyl ethers, allyl methacrylate, triallyl cyanurate, triallyl isocyanurate, ethylene dimethacrylate, diallyl maleate, maleic anhydride; maleimide compounds such as maleimide or N-phenyl (or alkyl) maleimide; and mixtures of these monomers. In an embodiment, the polymerizable alkenyl containing organic material is at least one selected from the group consisting of styrene, alpha-methylstyrene, acrylonitrile, methacrylonitrile, butyl acrylate, and (meth)acrylates, methyl methacrylate.

The silicone-acrylate impact modifier compositions disclosed herein can be prepared by emulsion polymerization techniques. In the first step of the technique, at least one silicone rubber monomer is reacted with at least one first graft link monomer at a temperature from about 30 °C to about 110 °C, and preferably from about 75 °C to about 95 °C, to form a silicone rubber latex. An effective amount of a surfactant can be used initially in the reactor as part of the agitated aqueous mixture, or it can be introduced with the silicone rubber monomers. Surfactants that can be used include acid catalyst-surfactants, for example, sulfonic acids, such as alkyl-, and alkaryl - arylsulfonic acids and mixtures of surface - active sulfonic acid salts with strong

mineral acids. Dodecylbenzenesulfonic acid is a preferred surfactant. In one embodiment of the method, the addition of monomers can be carried out batch wise or semi-continuously, and in a drop wise manner, over a period of up to 24 hours. The types of silicone rubber monomers and the first graft link monomers that can be used have been described previously. In another embodiment of the method, cyclooctamethyltetrasiloxane (hereinafter sometimes referred to as "D₄") and tetraethoxyorthosilicate (sometimes also referred to as a silicone cross linking monomer) are reacted with (gamma-methacryloxypropyl)methyldimethoxysilane (hereinafter sometimes referred to as "MAPMDMS") as a first graft link monomer to form silicone rubber particles. MAPMDMS facilitates chemical linking of acrylate chains onto the siloxane network. TEOS serves to form a weak cross-link in the silicone rubber particles. The average size of the silicone rubber particle depends on the cross-linking density. A higher cross-linking density generally results in a lowered particle size of the silicone rubber particles. In one embodiment, the method affords silicone rubber having an average particle size from about 100 nanometers to about 2 microns.

In the second step of the technique, at least one branched acrylate rubber monomer of the structure (I) is polymerized with the silicone rubber particles obtained in the first step to provide a latex comprising an emulsion polymerized silicone-acrylate rubber hybrid. In one embodiment, a branched acrylate rubber monomer of formula (I), such as isooctyl acrylate is polymerized with the silicone rubber particles in presence of a cross linking monomer, such as allylmethacrylate to get silicone-acrylate hybrid latex particles. Allylmethacrylate performs the dual function of cross linking the acrylate chains as well as acting as a graft linker (via the allyl group) for the grafting reaction in the third stage as described later in the disclosure. In another embodiment, a mixture of acrylate rubber monomers comprising the branched acrylate rubber monomers of structure (I) and linear acrylate rubber monomers, such as butyl acrylate can also be employed. The addition of the acrylate monomers to the silicone rubber latex occurs before, or concurrently with addition of a polymerization catalyst. The polymerization catalyst can be any material known in the art to initiate free radical polymerization, such as an alkali metal persulfate; or organic soluble radical initiators,

such as azobisisobutyronitrile, or an organic peroxide, such as benzoyl peroxide, dichlorobenzoyl peroxide, cumene hydroperoxide, and tert-butyl perbenzoate, to polymerize the branched acrylate rubber monomer and effect silicone-acrylate rubber hybrid formation. When an alkali metal persulfate catalyst is used, it is preferred that the persulfate be added over time to keep the vinyl polymerization running. This technique also minimizes degradation of the persulfate under the acid conditions present during the polymerization of the silicone rubber monomers. The emulsion polymerized silicone-acrylate rubber hybrid comprises about 95 parts to about 5 parts by weight of silicone rubber, and about 5 parts to about 95 parts by weight of polyacrylate rubber, per 100 parts by weight of said silicone-acrylate rubber hybrid.

In the third step, the latex comprising the emulsion polymerized silicone-acrylate rubber hybrid produced in the second step is reacted with at least one polymerizable alkenyl containing organic material and a second graft link monomer to form a graft silicone-acrylate rubber hybrid latex. In an embodiment, the polymerizable alkenyl containing organic material is polymerizable alkenyl containing organic material is at least one selected from the group consisting of styrene, alpha-methylstyrene, acrylonitrile, methacrylonitrile, and methyl methacrylate. The proportion of alkenyl organic containing material and the silicone-acrylate rubber hybrid latex can vary widely, such as for example, from about 0.15 part to about 3.0 part by weight of alkenyl organic containing material, per part of the silicone-acrylate rubber hybrid latex to form the graft silicone-acrylate rubber hybrid latex. When allyl methacrylate is used, in some situations, the residual allyl groups of allyl methacrylate resulting from the second step (described above) of the method itself acts as the second graft linker by facilitating the grafting of polymerizable alkenyl containing organic materials, such as styrene and acrylonitrile monomers onto the silicone-acrylate hybrid core. A variety of polymerizable alkenyl containing organic materials, such as those disclosed previously can be employed. When a mixture of styrene and acrylonitrile is used, then their weight ratio, in one embodiment, is between about 90:10 to about 50:50.

The latex particles of the graft silicone-acrylate rubber hybrid are separated from the aqueous phase through coagulation (by treatment with a coagulant) and dried to a fine powder to produce the silicone-acrylate rubber impact modifier composition.

The method described hereinabove can be generally used for producing the silicone-acrylate impact modifier having a particle size from about 100 nanometers to about 2 microns. In an embodiment, the method described hereinabove can be carried out batch wise or semi-continuously. In the batch wise process, all of the silicone rubber monomers are charged into the polymerization reactor containing water, and the polymerization reaction is then carried out. In the semi-continuous process, a portion of the mixture of the silicone rubber monomers are taken in water in the polymerization reactor, and subsequently the remaining portion of the silicone rubber monomer mixture is added over a period of time to form the silicone rubber latex particles. The semi-continuous process also includes the employment of mild, and/or low shear non-homogenizing conditions during the emulsion polymerization of the silicone rubber monomers.

The silicone rubber latex can also be synthesized through an emulsion polymerization route by using an additional homogenization step. The homogenization step generates particles having an average size of less than 500 nanometers with a substantially broad particle size distribution (hereinafter sometimes referred to as "PSD"). This creates performance issues in polymer resin blends comprising, since specific types of polymer resin systems require a certain type of average particle size and PSD for the silicone-acrylate rubber impact modifier compositions. For example, it is preferable to use silicone-acrylate impact modifier compositions having a relatively smaller average particle size and narrower (that is, closer to a mono-modal) PSD for polycarbonates, but a relatively broader (that is, closer to a bimodal) PSD for styrene-acrylonitrile copolymers. The method for forming the silicone-acrylate impact modifier compositions disclosed herein includes in an embodiment, a semi-continuous emulsion polymerization process without the homogenization step, where the particle size can be controlled such that one can achieve an average particle size of either less than or equal to about 500 nanometers, or greater than or equal to about 500 nanometers.

The silicone-acrylate impact modifier compositions disclosed hereinabove are useful materials for preparing polymer molding compositions having improved properties, such as stiffness, low temperature ductility, weatherability, and chemical resistance. The impact modifier compositions also confer unexpectedly, a higher melt volume rate to polymer and molding compositions during the processing step. A higher melt volume rate generally translates to easier processing of the polymer or molding compositions, which can be a significant benefit commercially.

The silicone-acrylate impact modifier can comprise from about 1 part to about 50 parts by weight, in one embodiment, and from about 5 parts to about 25 parts by weight, in another embodiment, per 100 parts by weight of the molding composition. More particularly, the silicone-acrylate impact modifier comprises from 7 parts to about 15 parts by weight, per 100 parts by weight of the molding composition.

The polymer comprising the polymer molding composition can be a thermoset polymer, a thermoplastic polymer, or combinations of both polymers. In an embodiment, the thermoplastic polymer is selected from the group consisting of polycarbonates, polyesters, polyestercarbonates, polyamides, polyethersulfones, polyetherimides, polyphenylene ethers, acrylate polymers, styrenic polymers, vinyl halide polymers, and blends of the foregoing polymers. Furthermore, the polymers comprising the molding compositions can be prepared by all methods known in the art. For example, suitable polycarbonates that can be used comprise those that are made by techniques, such as interfacial polymerization, melt polycondensation, bischloroformate polymerization with dihydric phenols and diols; and polymerization of dihydric phenols and diols with bisalicylate carbonates, such as bis(methylsalicylate)carbonate. More particularly, the thermoplastic polymer is selected from the group consisting of bisphenol A polycarbonate, 1,3-bis(4-hydroxyphenyl)-1-methyl-4-isopropylcyclohexane polycarbonate, polybutylene terephthalate, polyethylene terephthalate, acrylonitrile-styrene-acrylate core shell polymers, acrylonitrile-styrene-alpha-methylstyrene-acrylate core shell polymers, styrene-acrylonitrile copolymer, styrene-methacrylonitrile copolymer, acrylonitrile-butadiene-styrene copolymer, acrylonitrile-alpha-methylstyrene-butadiene copolymer, copolymers comprising structural units derived from isophthalic acid, terephthalic

acid, resorcinol, and bisphenol A (hereinafter sometimes referred to as "ITR"); and blends of the foregoing polymers. The ITR copolymers are a class of polymers that have carbonate and ester functionalities on the polymer backbone. They can be prepared by many generally known polymerization techniques known in the art. More particularly, the ITR copolymers are prepared by a stepwise interfacial polymerization process. A mixture of isophthaloyl chloride and terephthaloyl chloride is added to an excess of resorcinol in a two-phase system comprising aqueous alkali metal hydroxide and a halogenated hydrocarbon solvent, such as dichloromethane. The reaction is carried out in the presence of an acid scavenger, such as triethylamine to trap the hydrogen chloride generated during the reaction, while maintaining the pH of the system at about 7. The product of this reaction is an oligomeric polycarbonate having hydroxy group at both ends of the oligomer chain. In the next step, the oligomeric hydroxy-terminated polycarbonate is combined with an aromatic bisphenol, such as bisphenol A, and reacted with phosgene in a two phase system comprising aqueous alkali metal hydroxide and a halogenated hydrocarbon solvent, such as dichloromethane. A suitable acid scavenger, such as triethylamine is used to trap the hydrogen chloride by-product. A suitable amount of an appropriate monohydric phenol, such as phenol or para-cumylphenol is added as a chain stopper to cap the ends of the copolymer with phenyl or cumyl groups, respectively.

The polymer molding composition of the disclosure may also contain one or more antioxidants, heat stabilizers, ultraviolet (hereinafter referred to as "UV") stabilizers, fire retardants, and colorant compositions. The phenolic antioxidants useful in the instant compositions embrace a large family of compounds, examples of which are given below. Non-limiting examples of antioxidants that can be used in the molding composition of the disclosure include tris(2,4-di-tert-butylphenyl) phosphite, 3,9-di(2,4-di-tert-butylphenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane, 3,9-di(2,4-dicumylphenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane, tris(p-nonylphenyl) phosphite, 2,2',2''-nitriolo[triethyl-tris[3,3',5,5'-tetra-tertbutyl-1,1'-biphenyl-2'-diyl]phosphite], 3,9-distearoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane, dilauryl phosphite, 3,9-di[2,6-di-tert-butyl-4-methyl-phenoxy]-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane and tetrakis(2,4-di-tert-butylphenyl) 4,4'-

bis(diphenylene)phosphonite, distearyl pentaerythritol diphosphite, diisodecyl pentaerythritol diphosphite, 2,4, 6-tri-tert-butylphenyl-2-butyl-2-ethyl-1,3-propanediol phosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl)4,4'-biphenylene diphosphonite, (2,4,6-tri-tert-butylphenyl)-2-butyl-2-ethyl-1, 3-propanediol phosphite, tri-isodecyl phosphite, octadecyl 3,5-di-(tert)-butyl-4-hydroxyhydrocinnamate, and mixtures of phosphites containing at least one of the foregoing. Tris(2,4-di-tert-butylphenyl) phosphite, 2,4,6-tri-tert-butylphenyl-2-butyl-2-ethyl-1,3-propanediol phosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, and bis(2,4-dicumylphenyl) pentaerythritol diphosphite are especially preferred, as well as mixtures of phosphites containing at least one of the foregoing phosphites, and the like.

Non-limiting examples of processing aids that can be used include Doverlube® FL-599 (available from Dover Chemical Corporation), Polyoxyter® (available from Polychem Alloy Inc.), Glycolube P (available from Lonza Chemical Company), pentaerythritol tetrastearate, Metablen A-3000 (available from Mitsubishi Rayon), neopentyl glycol dibenzoate, and the like.

The molding compositions of the present disclosure are prepared by mechanically blending the components in conventional mixing equipment, e.g., a single or twin-screw extruder, Banbury mixer, or any other conventional melt compounding equipment. A vacuum may also be applied to the equipment during the compounding operation to further reduce odorous materials emanating from the composition. The order in which the components of the composition are mixed is not generally critical and may be readily determined by one of skill in this art.

The molding compositions described above are valuable for producing a variety of useful articles. In an embodiment, the articles comprise outdoor enclosures for electrical and telecommunications interface devices, smart network interface devices, exterior and interior vehicle parts, external housings for garden equipment, and exterior and interior building and construction parts. Non-limiting examples of articles include those comprising exterior and interior automotive parts, window frames, window profiles, gutters, downspouts, siding, automotive bumper, doorliner,

tailgate, interior parts, and fender; external housing for garden equipment, and snow scooter.

The molding compositions comprising different polymer resins and the silicone-acrylate impact modifier compositions disclosed herein possess superior properties, such as low temperature impact and ductility, as compared to the polymer resin compositions which comprises methyl methacrylate-butadiene-styrene block copolymer impact modifier.

The previously described embodiments of the present invention have many advantages, including the ability to prepare the silicone-acrylate impact modifier compositions, and new molding compositions having superior low temperature impact, ductility, and good weatherability.

While only certain features of the invention have been illustrated and described herein, many modifications and changes will occur to those skilled in the art. It is, therefore, to be understood that the appended claims are intended to cover all such modifications and changes as fall within the true spirit of the invention.

EXAMPLES

Notched Izod impact (hereinafter referred to as "NII") was measured by ISO 180 method, and expressed in kilojoules per meter square (kJ/m^2). Ductility at a chosen temperature was measured using the impact energy as well as stress whitening on the fracture surface. Generally, when stress whitening is observed, it indicates ductile failure mode. When stress whitening is not observed, it indicates a brittle failure mode. Ductility was measured by testing ten molded impact bars of a particular composition at a given temperature. The percent ductility is expressed as a percentage of impact bars that exhibited ductile failure mode.

Tensile strength was measured using ISO 527 method, and expressed in megapascals (Mpa). MVR was measured using ISO 1133 method (measured at 260 °C using a 2.16 kilogram force), and are expressed in cubic centimeters/10 minutes ($\text{cc}/10\text{min}$). HDT was measured using ISO 179 method, and are expressed in °C. Flexural modulus

(hereinafter designated as "FM") was measured using ISO 178 method, and is expressed in gigapascals (Gpa).

The weatherability tests were carried out by using an Atlas G 5000 accelerated weatherometer and ISO method SAE J1960. Test samples were exposed for about 1000 kilojoules to the xenon arc lamp in the weatherometer in accordance with the test method mentioned previously. The yellowness index (also called "YI") values were measured using a Gretag Mcbeth 7000A color spectrophotometer. The weatherability results are reported as yellowness index (also referred as "YI") values. Gloss measurements were carried out using Micro-TRI-Gloss instrument (available from BYK-Gardner, Germany). The gloss values are reported as percent gloss retention (also referred to as "%GR"), which indicates the percent of the original gloss retained after the weatherability test. The NI data was also measured at room temperature after the weatherability tests to determine the percent retention of notched Izod impact at room temperature (also referred to as "% NIR"). A lower YI, a higher % NIR retention, and a higher % GR retention would indicate better weatherability performance.

The thermoplastic resins used were polycarbonate, styrene-acrylonitrile copolymer, and blends of PC and SAN, PC/PBT blends (available commercially as "Xenoy[®]" from GE Plastics), and ITR-PC (available commercially from GE Plastics as Sollix[®]). Table 1 shows the loading of the various ingredients in parts by weight for preparing the molding compositions. The impact modifiers used for forming the polymer molding compositions are: MBS (methyl methacrylate – butadiene – styrene copolymer, commercially available from Rohm and Haas), S2001 (an impact modifier commercially available from Mitsubishi Rayon), and silicone-acrylate impact modifier compositions IM-1, IM-2, IM-3, IM-4, and IM-5, prepared using the general procedure described above. Comparative examples of molding compositions comprising IM-2, IM-5, MBS, and S2001 (a silicone acrylate impact modifier commercially available from Mitsubishi Rayon Company) were also prepared. "PETS" stands for pentaerythritol tetrastearate. MZP stands for monozinc phosphate.

Example 1. This Example describes the general procedure for preparing IM-4 silicone-acrylate impact modifier compositions by a semi-continuous emulsion polymerization process without a homogenization step.

A pre-emulsion mixture was prepared by combining D₄ (95.5 grams), tetraethylorthosilicate (2 grams), MPTMS (2.5 grams), dodecylbenzenesulfonic acid (0.5 grams), sodium dodecylbenzenesulfonate (1 gram), and deionized water (250 grams). About 20 percent by weight of the pre-emulsion mixture was charged together with deionized water (75 grams) into a five-necked reactor equipped with a condenser, nitrogen inlet, and a stirrer, and the resulting mixture was stirred for about 3 hours while maintaining the internal temperature at about 89 °C. The remainder of the pre-emulsion mixture was then fed continuously over a 3-hour period with continued stirring. After being stirred for about 2 hours at 89 °C, the resulting latex was cooled down to room temperature. The pH of the silicone rubber latex was neutralized to about 7 - 8 using 2-weight percent aqueous sodium hydroxide solution. The final silicone rubber latex thus obtained had about 40 percent total solids, and corresponds to a silicone rubber monomer conversion of about 89 – 91 percent.

The neutralized silicone rubber latex obtained above (70 grams) was mixed with deionized water (285 grams) and transferred to a four-necked round-bottomed flask equipped with a condenser, nitrogen inlet, and a mechanical stirring assembly. The contents of the reactor was heated to about 75 °C under a stream of nitrogen, followed by addition of a solution of deionized water containing potassium persulfate (0.33 grams weight percent relative to combined weights of isooctyl acrylate and triallyl cyanurate) and sodium bicarbonate (0.33 grams weight percent relative to combined weights of isooctyl acrylate and triallyl cyanurate). Then the internal temperature was allowed to reach 75°C. To this mixture was added over a period of about 2 hours, a mixture made up of isooctyl acrylate (29.4 grams) and triallyl cyanurate (0.6 grams). The polymerization reaction was allowed to continue for another 2 hours at 75 °C to furnish the silicone-acrylate rubber latex hybrid. The monomer conversion is found to be about 96 percent.

The silicone-acrylate rubber latex hybrid obtained from the previous step (75 grams) was introduced into a jacketed reaction flask with constant agitation, and heated to an internal temperature of about 70 °C. To this was added a solution made up of potassium persulfate (0.74 weight percent relative to combined weights of styrene and methyl methacrylate), sodium bicarbonate (0.74 weight percent relative to combined weights of styrene and methyl methacrylate), and water (220 grams). Then a pre-emulsion mixture of styrene (3.75 grams), methyl methacrylate (21.25 grams), sodium dodecylbenzenesulfonate (0.5 grams), and water (60 grams) was added to the reaction mixture, drop wise over a 3-hour period, while maintaining the reactor internal temperature at about 70 °C. After the drop wise addition, the temperature of the reaction was maintained for another 2 hours at 70 °C, and then cooled to room temperature. The monomer conversion in the resulting graft silicone-acrylate rubber hybrid latex is around 97 –98%.

The above graft silicone-acrylate rubber hybrid latex was coagulated by first slowly adding one part by weight of the latex to 1.6 parts by weight of an aqueous 0.5 - 0.75 weight percent calcium chloride solution maintained at 70⁰ C with mechanical agitation, then continuing the stirring for about 30 minutes, and then quenching the mixture by adding about 2 kilograms of water. The coagulated polymer product was filtered using a Buckner funnel, washed thoroughly with deionized water at ambient temperature, and dried in air oven maintained at 70 °C for at least 24 hours.

The above-described method was used for preparing various silicone-acrylate modifiers, identified as IM – 1, IM – 2, IM – 3, and IM – 5. The monomers used for preparing each of the impact modifiers is shown in Table 1. “MMA” stands for methyl methacrylate.

Table 1.

Impact Modifier	Silicone rubber monomers	First graft link monomer	Branched acrylate monomer(s)	Second graft link monomer	Polymerizable alkenyl containing organic material
IM-1	D ⁴ , TEOS	MAPDMMS	Isooctyl acrylate	Allyl methacrylate	Styrene/acrylonitrile
IM-2	D ⁴ , TEOS	MAPDMMS	n-butyl acrylate	Allyl methacrylate	Styrene/acrylonitrile
IM-3	D ⁴ , TEOS,	MPTMS	Isooctyl acrylate	Allyl methacrylate	Styrene/acrylonitrile
IM-4	D ⁴ , TEOS,	MPTMS	Isooctyl acrylate	TAC	MMA/styrene
IM-5	D ⁴ , TEOS,	MPTMS	2-ethylhexyl acrylate	TAC	MMA/styrene

Examples 2 – 5 and Comparative Examples 1 - 7. These examples describe molding composition formulations prepared using various combinations of the thermoplastic resins and the silicone-acrylate impact modifiers described previously. The formulations prepared are shown in Table 1. In the table “NU” means the particular ingredient was not used for making the formulation. These formulations were then used for preparing molding compositions as follows.

The formulations described above were extruded into pellets using a W&P ZSK25 twin-screw extruder and the conditions shown below.

Zone	Temperature (Deg C)
Feed Hopper (Zone 1)	100
Zone 2	200
Zone 3	230
Zone 4	240
Zone 5 (Nozzle)	250
Zone 6	260
Die	260

The pellets were injection molded into test specimens using an Engel 30-ton injection molder and the conditions shown below.

Zone	Temperature (Deg C)
Feed Hopper (Zone 1)	70
Zone 2	230
Zone 3	245
Zone 4	265
Zone 5 (Nozzle)	255
Mold	40 - 50

The properties were measured on the test specimens. Results are shown in Table 2. "NA" means data is not available.

Examination of the data shown in Example 2 of Table 2 indicates that the impact modifier prepared using isooctyl acrylate exhibits much better percent ductility at temperatures equal to or lower than -20°C , as compared with the corresponding molded part comprising MBS as the impact modifier (Comparative Example 3), S2001 impact modifier (Comparative Example 2), and n-butyl acrylate impact modifier (Comparative Example 1). Furthermore, the MVR value for the PC-SAN based molding composition comprising isooctyl acrylate is much higher than that comprising MBS (Comparative Example 3), indicating that impact modifiers prepared using isooctyl acrylate confer better processibility when they are incorporated in molding compositions. A higher MVR is desirable for better processibility. Moreover, PC-SAN based molding compositions retain the mechanical properties on par with those shown by molding compositions comprising MBS.

PC-PBT based molding composition of Example 3, comprising the impact modifier prepared using isooctyl acrylate as the branched acrylate monomer shows better

ductility at sub-zero temperatures while retaining mechanical properties as compared to the composition of Comparative Example 4 (which comprises the impact modifier prepared using 2-ethylhexyl acrylate) and Comparative Example 5 (using S2001 impact modifier), but similar to that of Comparative Example 6 (using MBS). Furthermore, the molding composition of Example 3 shows a significantly better MVR of 9.9 as compared to a value of 6.3 shown by the composition of Comparative Example 6. The molding composition of Example 3 also displays superior weatherability, as shown by the significantly lower YI and % GR, and % NIR values, as compared to the molding composition of Comparative Example 6, which contains MBS impact modifier.

The molding composition of Example 5 (comprising the isooctyl acrylate-based impact modifier) shows superior ductility at or below about -20°C below while retaining the mechanical properties, as compared to the composition of Comparative Example 7 which shows ductility only up to about -20°C .

While the disclosure has been illustrated and described in typical embodiments, it is not intended to be limited to the details shown, since various modifications and substitutions can be made without departing in any way from the spirit of the present disclosure. As such, further modifications and equivalents of the disclosure herein disclosed may occur to persons skilled in the art using no more than routine experimentation, and all such modifications and equivalents are believed to be within the spirit and scope of the disclosure as defined by the following claims. All Patents cited herein are incorporated herein by reference.

Table 1.

Ingredients used	Parts by weight in each formulation Example												
	2	1*	2*	3*	3	4	4*	5*	6*	7*	5		
SAN 576	21.8	21.8	26.8	24.8	NU	NU	NU	NU	NU	NU	NU	NU	NU
Phosphite stabilizer - 1	0.1	0.1	0.1	0.1	0.4	0.4	0.4	0.4	0.4				
PETS	0.3	0.3	0.3	0.3	NU	NU	NU	NU	NU	NU	NU	NU	NU
Phosphite stabilizer - 2	0.1	0.1	0.1	0.1	NU	NU	NU	NU	NU	NU	NU	NU	NU
MZP	NU	NU	NU	NU	0.1	0.1	0.1	0.1	0.1	0.1	NU	NU	NU
Phosphite stabilizer - 3	NU	NU	NU	NU	NU	NU	NU	NU	NU	0.03	0.03		
PC - 105	40.4	40.4	44.4	44.4	46.4	46.4	46.4	46.4	46.4	46.4	NU	NU	NU
PC - 175	17	17	17	17	NU	NU	NU	NU	NU	NU	NU	NU	NU
PBT - 315	NU	NU	NU	NU	12.9	9.4	12.9	13.9	12.9	12.9	NU	NU	NU
PBT - 195	NU	NU	NU	NU	26.7	23.2	26.7	27.9	26.7	26.7	NU	NU	NU
PET	NU	NU	NU	NU	0.3	0.3	0.3	0.3	0.3	0.3	NU	NU	NU
Sollx®	NU	NU	NU	NU	NU	NU	NU	NU	NU	86.7	80		
IM - 1	20	NU	NU	NU	NU	20	NU	NU	NU	NU	NU	NU	NU
IM - 2	NU	20	NU	NU	NU	NU	NU	NU	NU	NU	NU	NU	NU
IM - 4	NU	NU	NU	NU	13.3	NU	NU	NU	NU	NU	NU	NU	NU
IM - 5	NU	NU	NU	NU	NU	NU	13.3	NU	NU	NU	NU	NU	NU
IM - 3	NU	NU	NU	NU	NU	NU	NU	NU	NU	NU	20		
S2001	NU	NU	11.1	NU	NU	NU	NU	11.11	NU	NU	NU	NU	NU
ASA	NU	NU	NU	NU	NU	NU	NU	NU	NU	NU	NU	NU	NU
MBS	NU	NU	NU	13.3	NU	NU	NU	NU	13.3	13.3	NU	NU	NU

Table 2.

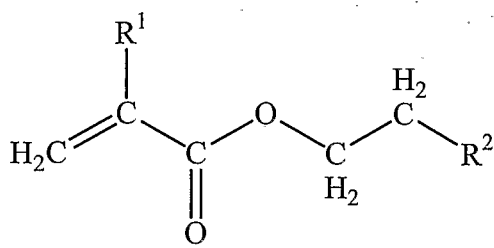
Formulation Example	NII (% ductility) at various temperatures					Tensile modulus	MVR	HDT	Flexural modulus	YI	% CB	% NI
	Ambient	0 °C	-20 °C	-30 °C	-40 °C							
2	54 (100)	52 ((100)	51 (100)	45 (100)	44 (100)	43.5	8.4	98	2.24	NA	NA	N ₂
3	59 (100)	46 (100)	43 (100)	32 (100)	29 (100)	43.6	9.9	68	2.1	32.7 7	84.6	79
4	53 (100)	26 (80)	16 (0)	NA (NA)	13 (0)	43.8	8.9	69.4	2.12	NA	NA	N ₂
5	65 (100)	57 (100)	51(100)	50 (100)	48 (100)	57	8.5	NA	2.19	NA	NA	N ₂
1*	47(100)	41 (100)	38 (100)	29 (0)	28 (0)	44.6	6	99.7	2.18	NA	NA	N ₂
2*	52 (100)	47 (100)	20 (0)	15 (0)	9 (0)	50.4	6.7	101	2.22	NA	NA	N ₂
3*	61 (100)	61 (100)	54 (60)	52 (40)	41 (0)	45.7	1.9	103	2.24	NA	NA	N ₂
4*	55 (100)	50 (100)	35 (40)	21 (0)	16 (0)	44.3	9.2	NA	2.2	NA	NA	N ₂
5*	56 (100)	47 (100)	21 (0)	21 (0)	16.5 (0)	36.9	16.6	73	1.88	NA	NA	N ₂
6**	53 (100)	50 (100)	50 (100)	46 (100)	42 (100)	41.7	6.3	71	2	41.1	69.5	72
7*	36 (100)	34 (100)	30 (100)	26 (20)	22 (0)	57.6	3	NA	2.22	NA	NA	N ₂

CLAIMS

1. A silicone-acrylate impact modifier composition, wherein said impact modifier composition comprises structural units derived from:

at least one silicone rubber monomer,

a branched acrylate rubber monomer having the formula:



wherein R^1 is selected from hydrogen and $\text{C}_1 - \text{C}_8$ linear and branched hydrocarbyl groups; and R^2 is a branched $\text{C}_3 - \text{C}_{16}$ hydrocarbyl group;

a first graft link monomer,

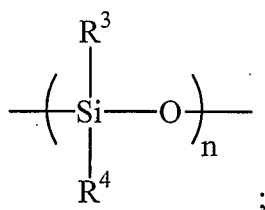
a polymerizable alkenyl-containing organic material, and

and a second graft link monomer.

2. The impact modifier composition of Claim 1, wherein R^1 is hydrogen and R^2 is at least one branched hydrocarbyl radical selected from 4-methylpentyl, 4-methylhexyl, and 5-methylhexyl.

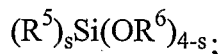
3. The impact modifier composition of Claim 1, wherein said silicone rubber monomer comprises:

at least one cyclic siloxane silicone rubber monomer of the formula:



wherein R^3 and R^4 are independently selected from hydrogen and $C_1 - C_{10}$ alkyl and aryl radicals; and "n" is an integer having a value from about 3 to about 20; and

at least one member selected from a trialkoxysilane and tetraalkoxysilane of the general formula:



wherein R^5 independently comprises hydrogen and $C_1 - C_{10}$ alkyl and aryl radicals; R^6 independently comprises $C_1 - C_4$ hydrocarbyl radicals; and "s" is an integer having a value from about 0 to about 1.

4. The impact modifier composition of Claim 1, wherein said silicone rubber monomer comprises:

at least one member selected from octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, and hexamethylcyclotrisiloxane; and

tetraethoxysilane.

5. The impact modifier composition of Claim 1, wherein said polymerizable alkenyl containing organic material comprises at least one aromatic vinyl monomer, olefinic nitrile; and branched and unbranched (meth)acrylate monomer.

6. The impact modifier composition of Claim 1, wherein said polymerizable alkenyl containing organic material is at least one selected from the group consisting of styrene, alpha-methylstyrene, acrylonitrile, methacrylonitrile, butyl acrylate, and methyl methacrylate.

7. The impact modifier composition of Claim 1, wherein said first graft link monomer comprises at least one of an (acryloxy)alkoxysilane, a (mercaptoalkyl)alkoxysilane, a vinylalkoxysilane, and an allylalkoxysilane.

8. The impact modifier composition of Claim 1, wherein said first graft link monomer comprises at least one of (gamma-

methacryloxypropyl)(dimethoxy)methylsilane, (3-mercaptopropyl)alkoxysilane, vinyltrimethoxysilane, and allyltrimethoxysilane.

9. The impact modifier composition of Claim 1, wherein said second graft link monomer is at least one polyethylenically unsaturated compound having at least one allyl group.

10. The impact modifier composition of Claim 1, wherein said second graft link monomer is at least one selected from the group consisting of allyl methacrylate, triallyl cyanurate, triallyl isocyanurate, and diallylmaleate.

11. A silicone-acrylate impact modifier composition, wherein said composition comprises structural units derived from:

a silicone rubber monomer comprising octamethylcyclotetrasiloxane and tetraethoxysilane;

a branched acrylate rubber monomer selected from the group consisting of iso-octyl acrylate, 6-methyloctyl acrylate, 7-methyloctyl acrylate, and combinations of the foregoing branched acrylate rubber monomers;

at least one first graft link monomer selected from the group consisting of (gamma-methacryloxypropyl)(dimethoxy)methylsilane and (3-mercaptopropyl)trimethoxysilane;

a polymerizable alkenyl-containing organic material comprising at least one of styrene, alpha-methylstyrene, acrylonitrile, methacrylonitrile, methyl methacrylate; and

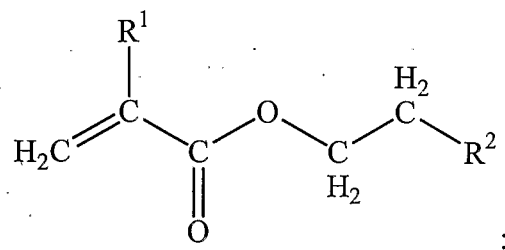
at least one second graft link monomer selected from the group consisting of allyl methacrylate, triallyl cyanurate, and triallyl isocyanurate.

12. The impact modifier composition of Claim 11, wherein said impact modifier composition further comprises structural units derived from at least one acrylate monomer selected from the group consisting of linear alkyl acrylates.

13. A molding composition comprising a polymer resin and a silicone-acrylate impact modifier composition, wherein said impact modifier composition comprises structural units derived from:

at least one silicone rubber monomer,

a branched acrylate rubber monomer having the formula:



wherein R^1 is selected from hydrogen and $\text{C}_1 - \text{C}_8$ linear and branched hydrocarbyl groups; and R^2 is a branched $\text{C}_3 - \text{C}_{16}$ hydrocarbyl group;

a first graft link monomer,

a polymerizable alkenyl-containing organic material, and

and a second graft link monomer;

wherein said molding composition has ductile-to-brittle transition temperature from about 0°C to about -60°C .

14. The molding composition of Claim 13, wherein said polymer is selected from thermoplastic and thermoset polymers.

15. The molding composition of Claim 14, wherein said thermoplastic polymer is selected from the group consisting of polycarbonates, polyesters, polyolefins, polyestercarbonates, polyamides, polyethersulfones, polyetherimides, polyphenylenes ether, acrylate polymers, styrenic polymers, vinyl halide polymers, and blends of the foregoing polymers.

16. The molding composition of Claim 14, wherein said thermoplastic polymer is bisphenol A polycarbonate, 1,3-bis(4-hydroxyphenyl)-1-methyl-4-

isopropylcyclohexane polycarbonate, polybutylene terephthalate, polyethylene terephthalate, acrylonitrile-styrene-acrylate core shell polymers, acrylonitrile-styrene-alpha-methylstyrene-acrylate core shell polymers, styrene-acrylonitrile copolymer, styrene-methacrylonitrile copolymer, acrylonitrile-butadiene-styrene copolymer, acrylonitrile-alpha-methylstyrene-butadiene copolymer, copolymers comprising structural units derived from isophthalic acid, terephthalic acid, resorcinol, and bisphenol A; and blends of the foregoing polymers.

17. The molding composition of Claim 13, wherein said impact modifier composition further comprises structural units derived from at least one acrylate monomer selected from the group consisting of linear alkyl acrylates.

18. An article of manufacture comprising the impact modifier composition of Claim 1.

19. The article of Claim 18, wherein said article comprises outdoor enclosures for electrical and telecommunications interface devices, smart network interface devices, exterior and interior vehicle parts, external housings for garden equipment, and exterior and interior building and construction parts.

20. The article of Claim 18, wherein said article comprises exterior and interior automotive parts, window frames, window profiles, gutters, downspouts, siding, automotive bumper, doorliner, tailgate, interior parts, and fender; external housing for garden equipment, and snow scooter.

21. A molding composition comprising a polymer resin and a silicone-acrylate impact modifier composition, wherein impact modifier composition comprises structural units derived from:

a silicone rubber monomer comprising octamethylcyclotetrasiloxane and tetraethoxysilane;

a branched acrylate rubber monomer selected from the group consisting of iso-octyl acrylate, 6-methyloctyl, 7-methyloctyl, and combinations of the foregoing branched acrylate rubber monomers;

at least one first graft link monomer selected from the group consisting of (gamma-methacryloxypropyl)(dimethoxy)methylsilane and (3-mercaptopropyl)trimethoxysilane;

a polymerizable alkenyl-containing organic material comprising at least one of styrene, alpha-methylstyrene, acrylonitrile, methacrylonitrile, methyl methacrylate; and

at least one second graft link monomer selected from the group consisting of allyl methacrylate and triallylcyanurate;

wherein said molding composition has ductile-to-brittle transition temperature from about 0 °C to about -60 °C.

22. The molding composition of Claim 21, wherein said impact modifier composition further comprises structural units derived from at least one acrylate monomer selected from the group consisting of linear alkyl acrylates.

23. A method for making a silicone-acrylate impact modifier composition, said method comprising:

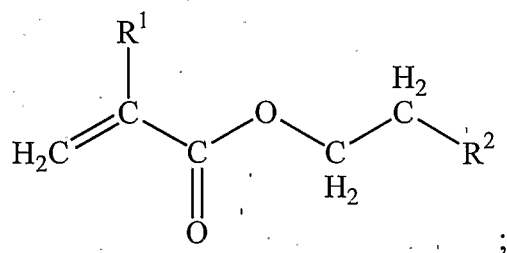
emulsion polymerizing at least one silicone rubber monomer and a first graft link monomer at a temperature from about 30 °C to about 110 °C to form a silicone rubber latex;

adding to said silicone rubber latex, at a pH of about 4 to about 9.5, and a temperature of about 20 °C to about 90 °C, at least one branched acrylate rubber monomer and a second graft link monomer to provide a latex comprising an emulsion polymerized silicone-acrylate rubber hybrid;

grafting said silicone-acrylate rubber hybrid with a polymerizable alkenyl containing organic material to form a graft silicone-acrylate rubber hybrid latex; and,

coagulating, washing, and drying said graft silicone-acrylate rubber hybrid latex to provide said silicone-acrylate rubber impact modifier composition;

wherein said at least one branched acrylate rubber monomer has the formula:



wherein R^1 is selected from hydrogen and $\text{C}_1 - \text{C}_8$ linear and branched hydrocarbyl groups; and R^2 is a branched $\text{C}_3 - \text{C}_{16}$ hydrocarbyl group.

24. The method of Claim 23, wherein said method further comprises adding to said silicone rubber latex, at least one acrylate monomer selected from the group consisting of linear alkyl acrylates.

25. The method of Claim 23, wherein said silicone rubber latex has a volume average particle size from about 100 nanometers to about 2 microns.

26. The method of Claim 23, wherein said polymerizable alkenyl containing organic material is at least one selected from the group consisting of styrene, alpha-methylstyrene, acrylonitrile, methacrylonitrile, and methyl methacrylate.