



There is provided by the present invention, a method for making an impact modifier for enhancing the weather resistance and low temperature impact strength of organic thermoplastic polymers, which method comprises,

(1) effecting the polymerization of silicone rubber monomers under semi- continuous emulsion polymerization conditions at a temperature of about 30°C to about 110°C, to provide for the formation of a silicone rubber latex having a volume average particle size in the range of from about 400 nm to about 2 microns,

(2) adding batchwise to the resulting silicone rubber latex of (1), while providing agitation at a pH of about 4 to about 9.5, and a temperature of about 20°C to about 90°C, a mixture comprising polymerizable acrylate rubber monomers to provide a latex comprising an emulsion polymerized silicone rubber-polyacrylate rubber hybrid having a weight proportion of from about 95 parts to about 5 parts of silicone rubber, and from about 5 parts to about 95 parts of polyacrylate rubber, and where the addition of the polymerizable acrylate rubber monomers into the silicone rubber latex occurs before, or concurrently with sufficient polymerization catalyst to effect acrylate rubber formation,

(3) grafting the emulsion polymerized silicone rubber-acrylate rubber hybrid latex of (2), with a sufficient amount of polymerizable alkenyl monomer to form a graft of the emulsion polymerized silicone rubber-polyacrylate rubber hybrid latex, and,

(4) coagulating, washing and drying the grafted emulsion polymerized latex of (3).

A further aspect of the present invention is directed to impact modifiers for enhancing the weather resistance and low temperature impact strength for thermoplastic polymers, wherein the impact modifiers comprise a comprising melt



extrudable polymerized alkenyl monomer graft of an emulsion polymerized silicone rubber-polyacrylate rubber hybrid wherein the hybrid is produced with polymerizable acrylate rubber monomers and arising from the initial use of an emulsion polymerized silicone rubber latex having a volume average particle size in the range of from about 400 nm to about 2 microns wherein the impact modifiers are made by the method described above.

An additional aspect of the present invention is directed to a moldable thermoplastic organic polymeric material having improved low temperature weather resistance and impact strength comprising an organic thermoplastic polymeric material and an effective amount of a silicone-acrylate impact modifier wherein the organic thermoplastic material comprises a styrene and acrylonitrile copolymer and a comprising the polymerized alkenyl material monomer graft wherein the graft comprises a melt extrudable styrene and acrylonitrile graft of an emulsion polymerized silicone rubber-polyacrylate rubber hybrid wherein the hybrid is produced with polymerizable acrylate rubber monomers and arising from the initial use of an emulsion polymerized silicone rubber latex having a volume average particle size in the range of from about 400 nm to about 2 microns wherein the latex is made under semi-continuous reaction conditions.

Still another aspect of the present invention is directed to a method for preparing a moldable thermoplastic organic polymeric material having improved weather resistance and low temperature impact strength, wherein the method which comprises mixing an organic thermoplastic polymeric material and an effective amount of a silicone-acrylate impact modifier, wherein the impact modifier comprises a comprising the polymerized alkenyl material graft of an emulsion polymerized silicone rubber-polyacrylate rubber hybrid wherein the hybrid is produced with polymerizable acrylate rubber monomers and arising from the initial use of an emulsion polymerized silicone rubber latex having a volume average particle size in the range of from about 400 nm to about 2 microns wherein the impact modifier is made by the method described above.

DETAILED DESCRIPTION OF THE INVENTION

In the practice of one form of the method of the invention, an emulsion polymerized silicone rubber latex is initially formed by semi-continuously adding to a reactor containing water, which is being agitated, such as stirring, at a temperature in the range of about 30°C to about 110°C, and preferably about 75°C to about 95°C, a mixture of silicone rubber monomers. The semi-

Graft silicone rubber-polyacrylate rubber latexes are coagulated in a 1.5% aqueous calcium chloride solution maintained at 85°C by slowly adding one part of the latex to one part of the aqueous calcium chloride solution. The resulting polymer solids are filtered, washed with distilled water at ambient
5 temperatures, and dried in a vacuum oven at room temperature for 24 hours, to form a fine powder. This powder is suitable as an impact modifier for a thermoplastic polymer.

For comparison, a commercially available styrene-acrylonitrile graft copolymer of a silicone rubber-polyacrylate rubber hybrid having a volume
10 average particle size in the range of about 280 nm was also evaluated. This material was Metablen S-2001, which is made by Mitsubishi Rayon Co. Ltd. The Metablen S-2001 silicone rubber impact modifier can be prepared in accordance with the method of Sasaki et al, U.S. patent 5,132,359.

A series of dry blends are prepared by respectively mixing 46 parts of SAN (a
15 75:25 by weight copolymer of styrene and acrylonitrile), 54 parts of a particular graft copolymer of example 1-3, and 1 part of Irganox 1076, a stabilizer of Ciba Geigy Corporation. The dry blends are extruded using a Welding Engineers 20 mm (0.02 m) twin-screw extruder at 450°F (232°C) set temperature, 400 rpm, and 15-17 lbs/hour (6.8 – 7.7 kg/hour) throughput, to obtain pellets. The pellets are injection molded to produce
20 0.125 in. (3.2 x 10⁻³ m) width test specimens utilizing an Engel 30 ton injection molder with a 450°F (232°C) barrel set temperature and 145°F (63°C) mold temperature.

The following Table, shows the Izod impact results derived from the respective thermoplastic SAN/silicone rubber-polyacrylate rubber graft blends. These Izod impact results are the average value obtained at room temperature from five test samples. A
25 Testing Machine Inc. Monitor/Impact instrument model 43-02 is used which has a 2 lb (0.9 kg) pendulum capacity.

Commercially available Metablen S-2001, available from Mitsubishi, is shown as a comparative example.

Impact Values of SAN Thermoplastic Blends

Graft Copolymer	Silicone Acrylate	RT Izod Impact
SAN(parts by weight)	Latex Particle Size (nm)	(ft-lb/in) (J/m)
[Metablen S-2001 blended to achieve 27% total rubber]	280	1.4 (75)
54/46	330	2.7 (144)
54/46	360	3.7 (198)
54/46	360	4.4 (235)
54/46	440	4.9 (262)
54/46	700	3.7 (198)
54/46	290/720	5.4 (289)

The above results show that the blending of an effective amount of the silicone rubber-polyacrylate rubber graft hybrids, or impact modifiers of the present invention, with a commercially available thermoplastic organic polymer, such as SAN, can provide thermoplastic compositions having improved impact strength as compared to the impact modifiers of the prior art.

The above results also show that valuable impact modifiers for thermoplastic polymers can be made by polymerizing acrylate rubber forming monomers in the presence of a silicone rubber latex having a volume average particle size of about 400 nm to 2 microns to form a silicone rubber-polyacrylate rubber hybrid latex, and the grafting of such latex with polymerizable alkenyl monomers, such as a styrene and acrylonitrile mixture.

2. A method in accordance with claim 1, where the silicone rubber monomers are octamethylcyclotetrasiloxane, tetraethoxysilane, and gamma-methacryloxypropyldimethoxymethylsilane.
3. A method in accordance with claim 1, where the polymerizable acrylate rubber monomers are butyl acrylate and allyl methacrylate.
4. A method in accordance with claim 1, where the polymerizable alkenyl containing organic material used in forming the graft is a mixture of styrene and acrylonitrile.
- ~~5. An impact modifier comprising a melt extrudable polymerized alkenyl monomer graft of an emulsion polymerized silicone rubber polyacrylate rubber hybrid arising from the initial use of an emulsion polymerized silicone rubber latex having a volume average particle size in the range of from about 400 nm to about 2 micron.~~
5. An impact modifier for enhancing the weather resistance and low temperature impact strength for thermoplastic polymers, wherein the impact modifier comprises a melt extrudable polymerized alkenyl monomer graft of an emulsion polymerized silicone rubber-polyacrylate rubber hybrid wherein the hybrid is produced with polymerizable acrylate rubber monomers and an emulsion polymerized silicone rubber latex having a volume average particle size in the range from about 400 nm to about 2 microns wherein the impact modifier is made by a method which comprises:
 - (1) effecting the polymerization of silicone rubber monomers under semi-continuous emulsion polymerization conditions at a temperature in a range between about 30°C and about 100 °C, to provide for the formation of the silicone rubber latex,

(2) adding batchwise to the resulting silicone rubber latex of (1), while providing agitation at a pH in a range between about 4 and about 9.5, and a temperature in a range between about 20 °C and about 90 °C, a mixture comprising polymerizable acrylate rubber monomers to provide a latex comprising an emulsion polymerized silicone rubber-acrylate rubber hybrid having a weight proportion in a range between about 95 parts and about 5 parts of silicone rubber, and in a range between about 5 parts and about 95 parts of polyacrylate rubber, and where the addition of the polymerizable acrylate rubber monomers into the silicone rubber latex occurs before, or concurrently with sufficient polymerization catalyst to effect acrylate rubber formation,

(3) grafting the emulsion polymerized silicone rubber-acrylate rubber hybrid latex of (2), with a sufficient amount of a polymerizable alkenyl containing organic material to form a graft of the emulsion polymerized silicone rubber-acrylate rubber hybrid latex, and,

(4) coagulating, washing, and drying the grafted emulsion polymerized latex of (3).

6. An impact modifier in accordance with claim 5, which is a mixture of melt extrudable polymerized alkenyl monomer grafts of emulsion polymerized silicone rubber-polyacrylate rubber hybrids, where at least one of the melt extrudable polymerized alkenyl monomer grafts is a graft of an emulsion polymerized silicone rubber-polyacrylate rubber hybrid arising from the use of produced with a silicone rubber latex having a volume average particle size within the range of from about 400 nm to about 2 microns.

7. A moldable thermoplastic organic polymeric material having improved weather resistance and low temperature impact strength comprising an organic thermoplastic ~~polymeric~~ material and an effective amount of a silicone-acrylate

impact modifier, wherein the organic thermoplastic material comprises a styrene and acrylonitrile copolymer and a comprising the polymerized alkenyl material graft wherein the graft comprises a melt extrudable styrene and acrylonitrile graft of an emulsion polymerized silicone rubber-polyacrylate rubber hybrid wherein the hybrid is produced with polymerizable acrylate rubber monomers and arising from the initial use of an emulsion polymerized silicone rubber latex having a volume average particle size in the range of from about 400 nm to about 2 microns wherein the latex is made under semi-continuous reaction conditions.

~~8. — A moldable thermoplastic organic polymeric material in accordance with claim 7, where the organic thermoplastic polymeric material is at least one polyester, polycarbonate, polyestercarbonate, polyamide, polyetherimide, polyphenylene ether, polystyrene, or a copolymer of styrene with acrylonitrile, methacrylonitrile, esters of acrylic acid, methacrylic acid or copolymers thereof.~~

~~9. — A moldable thermoplastic organic polymeric material in accordance with claim 7, comprising a styrene and acrylonitrile copolymer and a melt extrudable styrene and acrylonitrile graft of an emulsion polymerized silicone rubber-polyacrylate rubber hybrid arising from the initial use of an emulsion polymerized silicone rubber latex having a volume average particle size in the range of from about 400 nm to about 2 micron.~~

8. 10. A moldable thermoplastic organic polymeric material in accordance with claim 7, where the silicone-acrylate impact modifier is produced with arises from the initial use of a mixture of polymerized alkenyl monomer grafts of emulsion polymerized silicone rubber-polyacrylate rubber hybrids, where at least one of the emulsion polymerized silicone rubber-polyacrylate rubber hybrids is produced with arises from the initial use of an emulsion polymerized silicone rubber latex having a volume average particle size in the range of from about 400 nm to about 2 micron.

~~9. 11.~~ A moldable thermoplastic organic polymeric material in accordance with claim ~~8 10~~, where the silicone-acrylate impact modifier is produced with ~~arises from the initial use of~~ a bimodal mixture of polymerized alkenyl monomer grafts of emulsion polymerized silicone rubber-polyacrylate rubber hybrids.

~~10.12.~~ A moldable thermoplastic organic polymeric material in accordance with claim ~~8 10~~, where the polymerized alkenyl monomer graft arising from a silicone rubber-polyacrylate rubber hybrid having a volume average particle size in the range of from about 400 nm to about 2 micron is present in the mixture of polymerized alkenyl monomer grafts in at least a major proportion by weight.

~~11.13.~~ An article of manufacture made from the moldable thermoplastic organic polymeric material of claim 7.

~~12.14.~~ An article according to claim ~~11 13~~ comprising an outdoor enclosure for an electrical or telecommunications interface device.

~~13.15.~~ A method for preparing a moldable thermoplastic organic polymeric material having improved weather resistance and low temperature impact strength, wherein the method ~~which~~ comprises mixing an organic thermoplastic polymeric material and an effective amount of a silicone-acrylate impact modifier, wherein the impact modifier comprises a ~~comprising the~~ polymerized alkenyl material graft of an emulsion polymerized silicone rubber-polyacrylate rubber hybrid wherein the hybrid is produced with polymerizable acrylate rubber monomers and ~~arising from the initial use of~~ an emulsion polymerized silicone rubber latex having a volume average particle size in the range of from about 400 nm to about 2 microns wherein the impact modifier is made by a method which comprises:

(1) effecting the polymerization of silicone rubber monomers under semi-continuous emulsion polymerization conditions at a temperature in a range between about 30 °C. and about 100 °C, to provide for the formation of the silicone rubber latex,

(2) adding batchwise to the resulting silicone rubber latex of (1), while providing agitation at a pH in a range between about 4 and about 9.5, and a temperature in a range between about 20 °C and about 90 °C, a mixture comprising polymerizable acrylate rubber monomers to provide a latex comprising an emulsion polymerized silicone rubber-acrylate rubber hybrid having a weight proportion in a range between about 95 parts and about 5 parts of silicone rubber, and in a range between about 5 parts and about 95 parts of polyacrylate rubber, and where the addition of the polymerizable acrylate rubber monomers into the silicone rubber latex occurs before, or concurrently with sufficient polymerization catalyst to effect acrylate rubber formation,

(3) grafting the emulsion polymerized silicone rubber-acrylate rubber hybrid latex of (2), with a sufficient amount of a polymerizable alkenyl containing organic material to form a graft of the emulsion polymerized silicone rubber-acrylate rubber hybrid latex, and,

(4) coagulating, washing, and drying the grafted emulsion polymerized latex of (3).

14.16. The method of claim 13 45, wherein the organic thermoplastic polymeric material is at least one polyester, polycarbonate, polyestercarbonate, polyamide, polyetherimide, polyphenylene ether, polystyrene, or a copolymer of styrene with acrylonitrile, methacrylonitrile, esters of acrylic acid, methacrylic acid or copolymers thereof.