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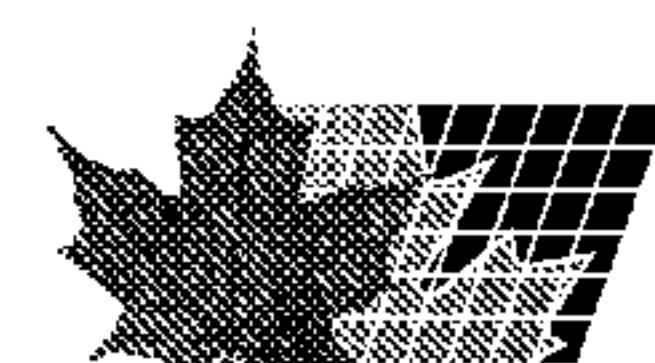
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(54) Titre : COPOLYMERE GREFFE, A BASE DE POLYORGANOSILOXANE

(54) Title: POLYORGANOSILOXANE GRAFT COPOLYMERS

(57) **Abrégé/Abstract:**

A polyorganosiloxane graft copolymer obtained by graft-polymerizing one or more kinds of monomer which have an ethylenically unsaturated bond and contain at least an epoxy group-containing vinyl monomer onto a compound rubber in which a polyorganosiloxane rubber and a polyalkyl (meth)acrylate rubber have been inseparably united with each other, and in which the component derived from the epoxy group-containing vinyl monomer occupies a proportion of 1 to 30 wt.% of the whole graft copolymer. This polyorganosiloxane graft copolymer is excellent in impact resistance, low-temperature characteristics and weather resistance, and also excellent in the bond strength to paint film applied thereto. This graft copolymer is also useful as adhesives, and particularly it exhibits excellent adhesion performance in depositing aromatic polymers such as polyesters (e.g. polyethylene terephthalate), polyphenylene oxides, polyphenylene sulfides, etc.



ABSTRACT OF THE DISCLOSURE

A polyorganosiloxane graft copolymer obtained by graft-polymerizing one or more kinds of monomer which have an ethylenically unsaturated bond and contain at least an epoxy group-containing vinyl monomer onto a compound rubber in which a polyorganosiloxane rubber and a polyalkyl (meth)acrylate rubber have been inseparably united with each other, and in which the component derived from the epoxy group-containing vinyl monomer occupies a proportion of 1 to 30 wt.% of the whole graft copolymer. This polyorganosiloxane graft copolymer is excellent in impact resistance, low-temperature characteristics and weather resistance, and also excellent in the bond strength to paint film applied thereto. This graft copolymer is also useful as adhesives, and particularly it exhibits excellent adhesion performance in depositing aromatic polymers such as polyesters (e.g. polyethylene terephthalate), polyphenylene oxides, polyphenylene sulfides, etc.

1 BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a polyorgano-siloxane graft copolymer excellent in impact resistance,
5 low-temperature characteristics and weather resistance, and further giving molded products excellent in bond strength to paint film applied thereon.

Description of the Related Art

As thermoplastic resins excellent in impact
10 resistance, low-temperature characteristics and weather resistance, a polyorganosiloxane graft copolymer obtained by graft-polymerizing a monomer having an ethylenically unsaturated bond (e.g. acrylonitrile, styrene) onto polyorganosiloxane rubber is disclosed in Japanese Patent
15 Application Kokai No. 61-106614. Also, a graft copolymer obtained by graft-polymerizing particular amounts of an epoxy group-containing vinyl monomer and other vinyl monomer onto a polyorganosiloxane polymer copolymerized with a graft-linking agent as copolymer component is
20 disclosed in Japanese Patent Application Kokai No. 2-138360.

However, the former graft copolymer disclosed in Japanese Patent Application Kokai No. 61-106614 has problems although it is excellent in impact resistance,

1 low-temperature characteristics and weather resistance.
Firstly, in the course of production of the graft
copolymer, an organosiloxane oligomer which is very
difficult to remove from the graft copolymer is produced
5 as by-product. Secondly, when the graft copolymer is
molded, this oligomer blooms out to the surface of the
molded product, so that when the molded product is
painted, the bond strength of the paint film is low.
Similarly, the graft copolymer disclosed in Japanese
10 Patent Application Kokai No. 2-138360 also has problems
although it is excellent in impact resistance, low-
temperature characteristics and weather resistance.
That is, the adhesion property of paint film applied to
the molded product of this graft copolymer is not of
15 very high level, and besides the above adhesion property
becomes quite poor as the amount of the polyorgano-
siloxane polymer in the graft copolymer becomes large.

SUMMARY OF THE INVENTION

In view of the situation mentioned above, the
20 present inventors have extensively studied to obtain a
resin excellent in impact resistance, low-temperature
characteristics and weather resistance as well as in
bond strength to paint film applied to the molded product
of the resin. As a result, the present inventors have
25 found that a polyorganosiloxane graft copolymer obtained
by graft-polymerizing one or more kinds of monomer which
have an ethylenically unsaturated bond and contain at

1 least an epoxy group-containing vinyl monomer onto a
compound rubber in which a polyorganosiloxane rubber
and a polyalkyl (meth)acrylate rubber have been inseparably
united with each other (hereinafter referred simply to
5 as compound rubber) and besides containing a particular
proportion of the component derived from the epoxy
group-containing vinyl monomer, satisfies all of the
performances described above. The present inventors thus
attained to the present invention.

10 Further, this polyorganosiloxane graft copolymer
is also useful as adhesives, and particularly it exhibits
excellent adhesion performance in laminating aromatic
polymers such as polyesters (e.g. polyethylene terephtha-
late), polyphenylene oxides, polyphenylene sulfides and
15 the like.

The gist of the present invention consists in
a polyorganosiloxane graft copolymer obtained by graft-
polymerizing one or more kinds of monomer which have
an ethylenically unsaturated bond and contain at least
20 an epoxy group-containing vinyl monomer onto a compound
rubber in which a polyorganosiloxane rubber and a
polyalkyl (meth)acrylate rubber have been inseparably
united with each other, and in which the component
derived from the epoxy group-containing vinyl monomer
25 occupies a proportion of 1 to 30 wt.% of the whole graft
copolymer.

1 DESCRIPTION OF THE PREFERRED EMBODIMENTS

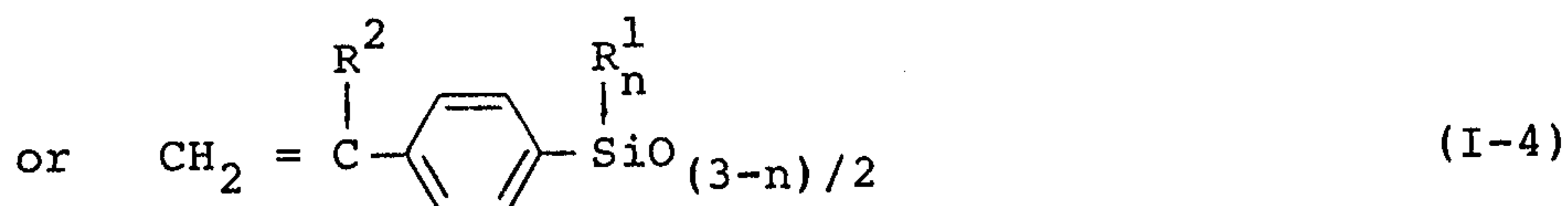
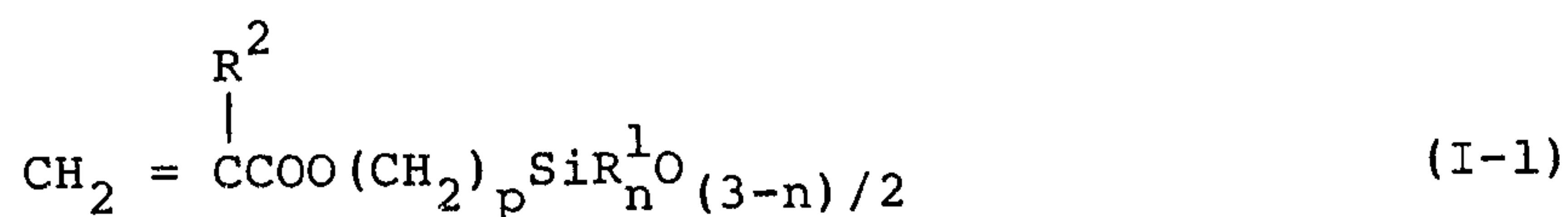
The polyorganosiloxane rubber constituting the graft copolymer of the present invention can be obtained in the form of fine particle by emulsion polymerization of organosiloxane, a crosslinking agent for polyorganosiloxane rubber (hereinafter referred to as crosslinking agent (I)) and if necessary a graft-linking agent for the polyorganosiloxane rubber (hereinafter referred to as graft-linking agent (I)).

As the organosiloxane used to prepare the polyorganosiloxane rubber, three or more-membered cyclic organosiloxanes are used, among which three to six-membered ones are preferably used. Examples of such the cyclic organosiloxane include hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, trimethyltriphenylcyclotrisiloxane, tetramethyltetraphenylcyclotetrasiloxane, octaphenylcyclotetrasiloxane and the like.

As the crosslinking agent (I) used to prepare the polyorganosiloxane rubber, trifunctional or tetrafunctional silanes, i.e. trialkoxyalkylsilanes or trialkoxyarylsilanes or tetraalkoxysilanes are used. Specific examples of such the crosslinking agent (I) include trimethoxymethylsilane, triethoxyphenylsilane, tetramethoxysilane, tetraethoxysilane, tetra-n-propoxysilane, tetrabutoxysilane and the like. Tetraalkoxysilanes are preferred, among which tetraethoxysilane is particularly

1 preferably used.

As the graft-linking agent (I) used if necessary to prepare the polyorganosiloxane rubber, compounds which can form a unit represented by either one of the formulae
 5 (I-1), (I-2), (I-3) and (I-4) are used:



wherein R^1 represents a methyl, ethyl, propyl or phenyl group, R^2 represents a hydrogen atom or a methyl group, n represents an integer of 0, 1 or 2, and p represents an integer of 1 to 6.

10 (Meth)acryloyloxyalkylsiloxane which can form the unit represented by the formula (I-1), because of its high grafting efficiency, can form graft chains effectively, so that it is advantageous in terms of development of impact resistance. Among (meth)acryloyloxy-
 15 alkylsiloxanes, methacryloyloxyalkylsiloxane is preferred. Specific examples of methacryloyloxyalkylsiloxane include β -methacryloyloxyethylmethoxymethylsilane, γ -methacryloyl-

1 oxypropylmethoxydimethylsilane, γ -methacryloyloxypropyl-
dimethoxymethylsilane, γ -methacryloyloxypropyltrimethoxy-
silane, γ -methacryloyloxypropylethoxydiethylsilane, γ -
methacryloyloxypropyldiethoxymethylsilane, δ -methacryloyl-
5 oxybutyldiethoxymethylsilane and the like. Vinylsiloxane
which can form the unit represented by the formula (I-2)
includes vinylmethyldimethoxysilane, vinyltrimethoxy-
silane and the like. Mercaptosiloxane which can form
the unit represented by the formula (I-3) includes γ -
10 mercaptopropyldimethoxymethylsilane, γ -mercaptopropyl-
trimethoxysilane, γ -mercaptopropyldiethoxyethylsilane
and the like. Compounds which can form the unit
represented by the formula (I-4) include p-vinylphenyl-
methyldimethoxysilane and the like.

15 The amount of the component derived from the
cyclic organosiloxane is 60 wt.% or more, preferably
70 wt.% or more of the polyorganosiloxane rubber.
The amount of the component derived from the crosslinking
agent (I) is 0.1 to 30 wt.% thereof, and that of the
20 component derived from the graft-linking agent (I) is
0 to 10 wt.%, preferably 0.1 to 10 wt.% thereof.

For producing the latex of this polyorgano-
siloxane rubber component, methods described, for
example, in USP No. 2891920, No. 3294725, etc. can be
25 used. In practicing the present invention, it is
preferred to produce the latex by the method in which a
mixed solution of organosiloxane, the crosslinking agent
(I) and if necessary the graft-linking agent (I) is

1 shear-mixed with water with, for example, a homogenizer
in the presence of a sulfonic acid emulsifier such as
an alkylbenzenesulfonic acid, an alkylsulfonic acid
and the like. As the sulfonic acid emulsifier, an
5 alkylbenzenesulfonic acid is preferably used because
it acts as an emulsifier for organosiloxane and at the
same time acts as a polymerization initiator. In this
case, it is preferred to use the metal salt of the
alkylbenzenesulfonic acid or an alkylsulfonic acid
10 together with the above sulfonic acid because the metal
salt has an effect to keep the emulsified state of the
polymer stable during the graft polymerization.

The compound rubber used in the present
invention is one which has such a structure that 1 to
15 99 wt.% of the polyorganosiloxane rubber component and
99 to 1 wt.% of the polyalkyl (meth)acrylate rubber
component have been inseparably united with each other,
and in which the total amount of both the components
is 100 wt.%.

20 When the composite rubber in which the amount
of the polyorganosiloxane rubber component exceeds 99
wt.% is used, the graft copolymer obtained gives molded
products having a reduced bond strength to paint film
applied thereon. When the composite rubber in which the
25 amount of the polyalkyl (meth)acrylate rubber component
exceeds 99 wt.% is used, the graft copolymer obtained
is low in impact resistance. Because of this, the
composite rubber used in the present invention needs to

1 be one in which the amount of any one of both the rubber
components constituting it is in a range of 1 to 99 wt.%,
provided that the total amount of both the components is
100 wt.%. Preferably, the amount of the polyorganosiloxane
5 rubber component is 5 to 80 wt.%, and that of the polyalkyl
(meth)acrylate rubber component is 95 to 20 wt.%.

For producing the composite rubber, it is desir-
able to use the emulsion polymerization method. That is,
it is desirable to firstly prepare the polyorganosiloxane
10 rubber by the emulsion polymerization method, and then to
subject the monomer for synthesizing the polyalkyl (meth)-
acrylate rubber to emulsion polymerization in the presence
of the polyorganosiloxane rubber latex prepared above.

The polyalkyl (meth)acrylate rubber component
15 constituting the composite rubber can be synthesized using
an alkyl (meth)acrylate, a crosslinking agent for the
polyalkyl (meth)acrylate rubber component (hereinafter
referred to as crosslinking agent (II)) and a graft-
linking agent for the same (hereinafter referred to as
20 graft-linking agent (II)).

The alkyl (meth)acrylate includes alkyl acrylates
(e.g. methyl acrylate, ethyl acrylate, n-propyl acrylate,
n-butyl acrylate, 2-ethylhexyl acrylate) and alkyl meth-
acrylates (e.g. hexyl methacrylate, 2-ethylhexyl meth-
25 acrylate, n-lauryl methacrylate). Among these, n-butyl
acrylate is preferably used.

As the crosslinking agent (II), polyfunctional
(meth)acrylates can be used. Specific examples thereof

1 include ethylene glycol dimethacrylate, propylene glycol
dimethacrylate, 1,3-butylene glycol dimethacrylate, 1,4-
butylene glycol dimethacrylate, allyl methacrylate and
the like.

5 As the graft-linking agent (II), compounds
having two kinds of unsaturated group different in
reactivity therebetween are used. Examples of such the
compound include allyl methacrylate, triallyl cyanulate,
triallyl isocyanulate and the like. The three allyl
10 groups of both triallyl cyanulate and triallyl iso-
cyanulate seem to have reactivity of the same level, but
after a first allyl group has reacted, second and third
allyl groups react in different reactivity from that of
the first one. Triallyl cyanulate and triallyl isocyanulate,
15 therefore, can be considered to have unsaturated groups
different in reactivity. In the case of allyl meth-
acrylate having two unsaturated groups, one of the
groups having lower reactivity also reacts in part during
polymerization to work as crosslinking site, but does
20 not react in full, so that the remaining unsaturated group
works as grafting site during the subsequent graft poly-
merization.

 These crosslinking agents (II) and graft-linking
agents (II) can be used alone or in combination of two
25 or more of them. Hereupon, it is desirable to cause allyl
methacrylate to own the functions of the both, i.e. to
use allyl methacrylate both as a crosslinking agent for
the polyalkyl (meth)acrylate rubber and as a graft-linking

1 agent for the same.

The amount of any one of these crosslinking agent (II) and graft-linking agent (II) used is 0.1 to 10 wt.% of the polyalkyl (meth)acrylate rubber component.

5 When allyl methacrylate is used as both the crosslinking agent (II) and the graft-linking agent (II), an effect that there is no need to further use other crosslinking agent (II) and graft-linking agent (II) is obtained by using the allyl methacrylate in amounts of 0.2 to 20 wt.%

10 of the polyalkyl (meth)acrylate rubber component.

The polyalkyl (meth)acrylate rubber component can be formed by adding the above alkyl (meth)acrylate, crosslinking agent (II) and graft-linking agent (II) to the polyorganosiloxane rubber latex and subjecting the

15 mixture to polymerization. These alkyl (meth)acrylate and both agents (II) may be added either in one portion or dropwise to the polymerization system.

With the progress of the polymerization, the polyalkyl (meth)acrylate rubber component formed by

20 the polymerization and the polyorganosiloxane rubber component are entangled and united with each other at the interface of the both to form a crosslinked network. Particularly, when the graft-linking agent (I) has been used in producing the polyorganosiloxane rubber component,

25 grafting of the polyalkyl (meth)acrylate rubber component onto the polyorganosiloxane rubber component also takes place. In either case, a compound rubber latex which cannot substantially be separated into both the rubber

1 components is obtained.

This compound rubber has a structure that the polyorganosiloxane rubber component and polyalkyl (meth)acrylate rubber component have been entangled in part,
5 united with each other and crosslinked in that state, so that it cannot be separated into both the rubber components by extraction with usual organic solvents such as acetone, toluene, etc.

A preferred compound rubber used in the present
10 invention is one in which the component derived from the cyclic organosiloxane in the polyorganosiloxane rubber component has a repeating unit of dimethylsiloxane, and the component derived from an alkyl (meth)acrylate in the polyalkyl (meth)acrylate rubber component has a
15 repeating unit of n-butyl acrylate.

The compound rubber thus obtained is graft-copolymerizable with a monomer having an ethylenically unsaturated bond, particularly a vinyl monomer.

The polyorganosiloxane graft copolymer of the
20 present invention is obtained by graft-polymerizing one or more kinds of monomer which have an ethylenically unsaturated bond and contain an epoxy group-containing vinyl monomer onto this composite rubber. If the graft copolymer is constituted so that the component derived
25 from the epoxy group-containing vinyl monomer is contained in amounts of 1 to 30 wt.%, preferably 2 to 30 wt.% of the graft copolymer, other monomer having an ethylenically unsaturated bond than the epoxy group-containing vinyl

1 monomer may be graft-polymerized together.

The epoxy group-containing vinyl monomer includes glycidyl methacrylate, glycidyl acrylate, vinyl glycidyl ether, allyl glycidyl ether, glycidyl ether
5 of hydroxyalkyl (meth)acrylate, glycidyl ether of polyalkylene glycol (meth)acrylate, glycidyl itaconate and the like. Among these, glycidyl methacrylate is preferably used.

The monomer having an ethylenically unsaturated
10 bond copolymerizable with the epoxy group-containing vinyl monomer includes aromatic alkenyl compounds (e.g. styrene, halogen-substituted styrene, α -methylstyrene, vinyltoluene, vinylpyridine), methacrylates (e.g. methyl methacrylate, 2-ethylhexyl methacrylate), acrylates
15 (e.g. methyl acrylate, ethyl acrylate, butyl acrylate) and vinyl cyanide compounds (e.g. acrylonitrile, methacrylonitrile). These monomers are used alone or in combination of two or more of them.

The proportion of the component derived from
20 the grafted monomer having an ethylenically unsaturated bond, particularly grafted vinyl monomer in the graft copolymer is preferably 5 to 95 wt.%, more preferably 10 to 90 wt.%, most preferably 10 to 50 wt.% when the weight of the graft copolymer is taken as 100%.

25 Also, it is desirable for the polyorganosiloxane graft copolymer of the present invention to have an average particle size ranging from 0.08 to 0.6 μm . When the average particle size is less than 0.08 μm , it becomes

1 difficult to obtain sufficient impact strength, and when
it is larger than 0.6 μm , there is a fear that the graft
copolymer obtained gives molded products having a poor
surface appearance.

5 The polyorganosiloxane graft copolymer having
such the average particle size can be obtained by one-
stage or multi-stage emulsion graft-polymerization of
one or more kinds of monomer containing the epoxy group-
containing vinyl monomer in the presence of the above
10 compound rubber latex. When the multi-stage graft-
copolymerization is carried out using the epoxy group-
containing vinyl monomer and other monomer than the one
above as the aforementioned one or more kinds of monomer
containing the epoxy group-containing vinyl monomer, it
15 is desirable to add the epoxy group-containing vinyl
monomer at the last stage of the graft polymerization.

 In this graft polymerization, the component
alone corresponding to the branch of the graft copolymer,
which refers herein to a component derived from one or
20 more kinds of monomer which have an ethylenically un-
saturated bond and contain the epoxy group-containing
vinyl monomer, polymerizes by itself without grafting
onto a trunk component which refers herein to the
composite rubber, to produce the so-called free polymer
25 as by-product. In other words, a mixture of the desired
graft copolymer and the free polymer is obtained by the
graft polymerization. In the present invention, however,
this mixture is referred to as "graft copolymer".

1 The polyorganosiloxane graft copolymer of
the present invention is excellent in impact resistance,
low-temperature characteristics and weather resistance,
and when molded and painted, gives molded products
5 excellent in adhesion to paint film. Further, it is also
useful as adhesives, being able to be used for adhesion
of metals (e.g. aluminum), wood, paper, glass, etc. and
adhesion of various structural laminates. Particularly,
it is useful as reactive hot melt adhesives for adhesion
10 of aromatic polymer molded products.

 The above aromatic polymer includes aromatic
polyesters such as polyethylene terephthalate, poly-
butylene terephthalate, polyethylene terephthalate·iso-
phthalate, polyethylene-2,6-naphthalenedicarboxylate,
15 polyphenylene terephthalate, bisphenol A/terephthalic
acid polycondensate, bisphenol A/terephthalic acid/
isophthalic acid copolycondensate, etc., substituted
or unsubstituted polyphenylene oxide and substituted or
unsubstituted polyphenylene sulfide. Among these,
20 polyethylene terephthalate, polybutylene terephthalate,
substituted or unsubstituted polyphenylene oxide and
substituted or unsubstituted polyphenylene sulfide can
be given as a preferred object to be adhered with the
graft copolymer of the present invention.

25 The present invention will be illustrated
in more detail with reference to the following examples
and comparative examples, but it is not to be interpreted
as being limited thereto.

1 In the examples and comparative examples, "part"
and "percent (%)" mean "part by weight" and "wt.%",
respectively, unless otherwise stated. The physical
properties in the above examples were measured by the
5 following methods.

Adhesion property of paint film:

A flat plate was prepared by molding the poly-
organosiloxane graft copolymer, and its surface was
coated with a two-component acrylic urethane paint
10 (reaction product of tolylenediisocyanate with acrylic
polyol). After drying, 11 parallel grooves were cut into
the coated surface at intervals of 1 mm in one direction,
and the same procedure was repeated in the direction
perpendicular thereto, thereby forming 100 grid patterns
15 of 1 mm². A cellophane adhesive tape was applied over
the cross-hatched area and peeled off the area in the
vertical direction to the surface of the flat plate,
and the number of the paint films peeled off the area
was counted. The adhesion property of the paint film
20 was evaluated according to the following standard:

The number of peeled paint films

◎	10 or less
○	11 to 20
Δ	21 to 40
X	41 or more

1 Izod impact strength:

Measured according to ASTM D-256 using a test piece with a 1/4" notch.

Weather resistance:

- 5 The test piece was exposed for 1000 hours in a sunshine weatherometer, and the change of the color was examined by visual assessment. The weather resistance was evaluated according to the following standard:

○	No change
△	Slight change to yellow
X	Change to yellow

Average particle size:

- 10 Measured according to the quasi-elastic light scattering method (MALVERN SYSTEM 4600™; measurement temperature, 25°C; angle of scattering, 90 degrees) using an aqueous dilute solution of the latex as sample solution.

15 Example 1

- Two parts of tetraethoxysilane, 0.5 part of γ -methacryloyloxypropyldimethoxymethylsilane and 97.5 parts of octamethylcyclotetrasiloxane were mixed to obtain 100 parts of a siloxane mixture. One part of sodium dodecylbenzenesulfonate and 1 part of dodecylbenzenesulfonic acid were dissolved in 200 parts of distilled water, and to the resulting solution was added 100 parts of the above siloxane mixture. The resulting
- 20

1 mixture was preliminarily stirred at 10000 rpm with a
homomixer and then emulsified with a homogenizer under
a pressure of 300 kg/cm^2 to obtain an organosiloxane
latex. This latex was transferred to a separable flask
5 equipped with a condenser and a stirring blade, and
heated at 80°C for 5 hours with stirring and mixing and
then allowed to stand at 20°C for 48 hours. Thereafter,
this latex was neutralized to a pH of 7.0 with an aqueous
sodium hydroxide solution to complete polymerization.
10 Thus, a polyorganosiloxane latex (hereinafter referred
to as POS-1) was obtained. The conversion of the
siloxane mixture to the polyorganosiloxane rubber was
89.7%, and the average particle size of the polyorgano-
siloxane rubber was $0.16 \mu\text{m}$.
15 One hundred and fifty parts of POS-1 was
sampled and put in a separable flask equipped with a
stirrer. After 185 parts of distilled water was added
and the atmosphere of the flask was replaced by a
nitrogen gas, the contents of the flask were heated
20 to 50°C . At this temperature, a mixed solution of
45 parts of n-butyl acrylate, 0.9 part of allyl meth-
acrylate and 0.108 part of tert-butyl hydroperoxide
was added, after which stirring was continued for 30
minutes to allow these components to soak into the
25 polyorganosiloxane rubber particles. Thereafter, a
mixed solution of 0.001 part of ferrous sulfate, 0.003
part of disodium ethylenediaminetetraacetate, 0.108
part of Rongalite (sodium formaldehyde sulfoxylate)

1 and 10 parts of distilled water was added to carry out
radical polymerization. The reaction mixture was kept
at an inner temperature of 70°C for 2 hours to complete
the polymerization. Thus, a compound rubber latex was
5 obtained. The conversion of the butyl acrylate rubber
component was 98.8%.

Forty parts of this compound rubber latex
was sampled, and 260 parts of distilled water and 0.5
part of sodium dodecylbenzenesulfonate were added
10 thereto. Subsequently, a mixed solution of 10 parts
of glycidyl methacrylate, 24 parts of acrylonitrile, 56
parts of styrene and 0.216 part of tert-butyl hydro-
peroxide was added and the atmosphere of the flask
was replaced by a nitrogen gas, then the contents of the
15 flask were heated to 50°C. Thereafter, a mixed solution
of 0.001 part of ferrous sulfate, 0.003 part of disodium
ethylenediaminetetraacetate, 0.108 part of Rongalite™
and 10 parts of distilled water was further added to
carry out radical polymerization. Thereafter, the reac-
20 tion mixture was kept at an inner temperature of 70°C for
4 hours to complete graft polymerization onto the com-
pound rubber to obtain a graft copolymer latex. The
conversion of glycidyl methacrylate, acrylonitrile and
styrene was 97.5%, and the average particle size of the
25 graft copolymer latex was 0.20 μm. The resulting graft
copolymer latex was coagulated with an aqueous calcium
chloride solution, and the resulting coagulated product
was filtered off and dried to obtain the dry powder of

1 a polyorganosiloxane graft copolymer (hereinafter
referred to as S-1).

S-1 was pelletized by extruding it through an
extruder at a barrel temperature of 230°C and molded
5 into a flat plate of 100 mm x 100 mm x 3 mm with an
injection molding machine ("IS-100"™ produced by Toshiba
Machine Co., Ltd.) at a cylinder temperature of 230°C
and a mold temperature of 60°C. The surface of this
flat plate was degreased with methanol and painted with
10 an acrylicurethane paint. The peeling test of this
paint film was carried out. Under the same injection
molding conditions as above, a test piece for evaluation
of impact strength was prepared, and the impact resistance
was evaluated. The results are shown in Table 1.

15 Example 2

A polyorganosiloxane graft copolymer of 0.20
μm in average particle size (hereinafter referred to as
S-2) was obtained in the same manner as in Example 1
except that as a monomer mixture to be graft-polymerized
20 onto the compound rubber latex, a mixture of 10 parts
of glycidyl methacrylate and 80 parts of styrene was
used in place of the mixture of 10 parts of glycidyl
methacrylate, 24 parts of acrylonitrile and 56 parts
of styrene. The resulting graft copolymer was evaluated
25 in the same manner as in Example 1. The results are
shown in Table 1.

1 Comparative Example 1

Thirty three parts of POS-1 obtained according to Example 1 was sampled, and 267 parts of distilled water and 0.5 part of sodium dodecylbenzenesulfonate were added thereto. Subsequently, a mixed solution of 10 parts of glycidyl methacrylate, 24 parts of acrylonitrile, 56 parts of styrene and 0.216 part of tert-butyl hydroperoxide was added and the atmosphere of the flask was replaced by a nitrogen gas. Then, the contents of the flask were heated to 50°C. Thereafter, a mixed solution of 0.001 part of ferrous sulfate, 0.003 part of disodium ethylenediaminetetraacetate, 0.108 part of Rongalite™ and 10 parts of distilled water was further added to carry out radical polymerization. Thereafter, the reaction mixture was kept at an inner temperature of 70°C for 4 hours to complete graft polymerization onto the polyorganosiloxane rubber to obtain a graft copolymer latex. The conversion of glycidyl methacrylate, acrylonitrile and styrene was 96.3%, and the average particle size of the graft copolymer latex was 0.21 μm. The resulting graft copolymer latex was coagulated with an aqueous calcium chloride solution, and the coagulated product was filtered off and dried to obtain the dry powder of a polyorganosiloxane graft copolymer (hereinafter referred to as S-3).

S-3 was evaluated in the same manner as in Example 1. The results are shown in Table 1.

1 Example 3

A polyorganosiloxane graft copolymer of 0.20 μm in average particle size (hereinafter referred to as S-4) was obtained in the same manner as in Example 1 except that as a monomer mixture to be graft-polymerized onto the compound rubber, a mixture of 20 parts of glycidyl methacrylate, 21 parts of acrylonitrile and 49 parts of styrene was used in place of the mixture of 10 parts of glycidyl methacrylate, 24 parts of acrylonitrile and 56 parts of styrene. The resulting graft copolymer was evaluated in the same manner as in Example 1. The results are shown in Table 1.

Example 4

A polyorganosiloxane graft copolymer (hereinafter referred to as S-5) was obtained in the same manner as in Example 1 except that the amount of the compound rubber latex sampled for graft copolymerization onto the compound rubber was 80 parts, the amount of distilled water to be added thereto was 230 parts, and that a mixture of 10 parts of glycidyl methacrylate, 21 parts of acrylonitrile and 49 parts of styrene was used as a monomer mixture to be graft-polymerized. The resulting graft copolymer was evaluated in the same manner as in Example 1. The results are shown in Table 1. The conversion of glycidyl methacrylate, acrylonitrile and styrene was 98.1%, and the average particle size of the graft copolymer latex was 0.21 μm .

1 Example 5

A polyorganosiloxane graft copolymer (hereinafter referred to as S-6) was obtained in the same manner as in Example 1 except that the amount of the compound
5 rubber latex sampled for graft copolymerization onto the compound rubber was 120 parts, the amount of distilled water to be added thereto was 200 parts, and that a mixture of 10 parts of glycidyl methacrylate, 18 parts of acrylonitrile and 42 parts of styrene was used as a
10 monomer mixture to be graft-polymerized. The resulting graft copolymer was evaluated in the same manner as in Example 1. The results are shown in Table 1. The conversion of glycidyl methacrylate, acrylonitrile and styrene was 98.1%, and the average particle size of the
15 graft copolymer latex was 0.20 μm .

Comparative Example 2

Ninety nine parts of POS-1 obtained in the same manner as in Example 1 was sampled, and 218 parts of distilled water and 0.5 part of sodium dodecylbenzene-
20 sulfonate were added thereto. Subsequently, a mixed solution of 10 parts of glycidyl methacrylate, 18 parts of acrylonitrile, 42 parts of styrene and 0.216 part of tert-butyl hydroperoxide was added to allow these components to soak into the polyorganosiloxane rubber particles.
25 Thereafter, the atmosphere of the flask was replaced by a nitrogen gas, and the contents of the flask were heated to 50°C. Subsequently, a mixed solution of 0.001

1 part of ferrous sulfate, 0.003 part of disodium ethylenediaminetetraacetate, 0.108 part of Rongalite and 10 parts of distilled water was further added to carry out graft polymerization onto the polyorganosiloxane rubber.

5 Thereafter, the reaction mixture was kept at an inner temperature of 70°C for 4 hours to complete the graft polymerization. Thus, the latex of a polyorganosiloxane graft copolymer was obtained. The resulting graft copolymer latex was coagulated with an aqueous calcium

10 chloride solution, and the coagulated product was filtered off and dried to obtain the dry powder of a polyorganosiloxane graft copolymer (hereinafter referred to as S-7). S-7 was evaluated in the same manner as in Example 1. The results are shown in Table 1. The

15 conversion of glycidyl methacrylate, acrylonitrile and styrene was 96.3%, and the average particle size of the graft copolymer latex was 0.20 μm .

Example 6

A polyorganosiloxane graft copolymer (hereinafter referred to as S-8) was obtained in the same manner as in Example 1 except that the amount of the compound rubber latex sampled for graft copolymerization onto the compound rubber was 160 parts, the amount of distilled water to be added thereto was 170 parts, and that a

25 mixture of 10 parts of glycidyl methacrylate, 15 parts of acrylonitrile and 35 parts of styrene was used as a monomer mixture to be graft-polymerized. The resulting

1 graft copolymer was evaluated in the same manner as
in Example 1. The results are shown in Table 1. The
conversion of glycidyl methacrylate, acrylonitrile and
styrene was 98.1%, and the average particle size of the
5 graft copolymer latex was 0.20 μm .

Example 7

A polyorganosiloxane graft copolymer (herein-
after referred to as S-9) was obtained in the same manner
as in Example 1 except that the amount of the compound
10 rubber latex sampled for graft copolymerization onto
the compound rubber was 200 parts, the amount of
distilled water to be added thereto was 140 parts, and
that a mixture of 10 parts of glycidyl methacrylate,
12 parts of acrylonitrile and 28 parts of styrene was
15 used as a monomer mixture to be graft-polymerized. The
resulting graft copolymer was evaluated in the same
manner as in Example 1. The results are shown in Table
1. The conversion of glycidyl methacrylate, acrylonitrile
and styrene was 97.8%, and the average particle size of
20 the graft copolymer latex was 0.18 μm .

Example 8

A polyorganosiloxane graft copolymer (herein-
after referred to as S-10) was obtained in the same
manner as in Example 1 except that the amount of the
25 compound rubber latex sampled for graft copolymerization
onto the compound rubber was 240 parts, the amount of

1 distilled water to be added thereto was 110 parts, and
that a mixture of 10 parts of glycidyl methacrylate, 9
parts of acrylonitrile and 21 parts of styrene was used
as a monomer mixture to be graft-polymerized. The
5 resulting graft copolymer was evaluated in the same manner
as in Example 1. The results are shown in Table 1. The
conversion of glycidyl methacrylate, acrylonitrile and
styrene was 98.2%, and the average particle size of the
graft copolymer latex was 0.18 μm .

10 Comparative Example 3

Two hundreds parts of POS-1 obtained in the
same manner as in Example 1 was sampled, and 150 parts
of distilled water and 0.5 part of sodium dodecylbenzene-
sulfonate were added thereto. Subsequently, a mixed
15 solution of 10 parts of glycidyl methacrylate, 9 parts
of acrylonitrile, 21 parts of styrene and 0.15 part of
tert-butyl hydroperoxide was added to allow these
components to soak into the polyorganosiloxane rubber
particles. After the atmosphere of the reactor was
20 replaced by a nitrogen gas, the reaction mixture was
heated to 50°C, and at this temperature, a mixed solution
of 0.001 part of ferrous sulfate, 0.003 part of disodium
ethylenediaminetetraacetate, 0.1 part of Rongalite™ and
10 parts of distilled water was added to carry out graft
25 polymerization onto the polyorganosiloxane rubber.
Thereafter, the reaction mixture was kept at an inner
temperature of 70°C for 4 hours to complete the graft

1 polymerization. Thus, the latex of a polyorganosiloxane
graft copolymer was obtained. The resulting graft
copolymer latex was coagulated with an aqueous calcium
chloride solution, and the coagulated product was
5 filtered off and dried to obtain the dry powder of a
polyorganosiloxane graft copolymer (hereinafter referred
to as S-11). S-11 was evaluated in the same manner
as in Example 1. The results are shown in Table 1.
The conversion of glycidyl methacrylate, acrylonitrile
10 and styrene was 96.5%, and the average particle size of
the graft copolymer latex was 0.21 μm .

Comparative Example 4

A polyorganosiloxane graft copolymer (herein-
after referred to as S-12) was obtained in the same
15 manner as in Example 1 except that as a monomer mixture
to be graft-polymerized onto the compound rubber latex,
a mixture of 27 parts of acrylonitrile and 63 parts of
styrene was used in place of the mixture of 10 parts
of glycidyl methacrylate, 24 parts of acrylonitrile and
20 56 parts of styrene. The resulting graft copolymer
was evaluated in the same manner as in Example 1. The
results are shown in Table 1.

Table 1

	Rubber composition (part) (PDMS/PBA)	Composition of monomers to be grafted (parts)			Izod impact strength		Weather resistance	Adhesion property of paint film
		GMA	AN	St	23°C	0°C		
Example 1	5/5	10	24	56	15	13	○	◎
Example 2	5/5	10	-	80	14	13	○	◎
Comparative Example 1	10/0	10	24	56	17	16	○	○
Example 3	5/5	20	21	49	15	14	○	◎
Example 4	10/10	10	21	49	38	33	○	◎
Example 5	15/15	10	18	42	49	42	○	◎
Comparative Example 2	30/0	10	18	42	51	50	○	○
Example 6	20/20	10	15	35	53	49	○	◎
Example 7	25/25	10	12	28	65	58	○	◎
Example 8	30/30	10	9	21	N.B. ²⁾	N.B.	○	○

- to be continued -

Table 1 (cont'd.)

Comparative Example 3	60/0	10	9	21	N.B.	N.B.	○	X
Comparative Example 4	5/5	-	27	63	14	12	○	X

(1) In the above table:

- PDMS : Polydimethylsiloxane
- PBA : Polybutyl acrylate
- GMA : Glycidyl methacrylate
- AN : Acrylonitrile
- St : Styrene

(2) N.B. means that the test piece was not broken.

1 Example 9

Two hundred and ninety parts of the composite rubber latex obtained according to Example 1 was sampled and put in a separable flask equipped with a stirrer.

5 The atmosphere of the flask was replaced by a nitrogen gas. Then, the contents of the flask were heated to 50°C. Thereafter, a mixed solution of 0.00025 part of ferrous sulfate, 0.00075 part of disodium ethylenedi-aminetetraacetate, 0.025 part of Rongalite™ and 10 parts

10 of distilled water was added. A mixed solution of 10 parts of glycidyl methacrylate and 0.024 part of tert-butyl hydroperoxide was dropwise added thereto over 30 minutes. The reaction mixture was kept at an inner temperature of 70°C for 4 hours to carry out graft

15 polymerization onto the compound rubber. Thus, the latex of a polyorganosiloxane graft copolymer (hereinafter referred to as S-13) was obtained. This graft copolymer latex was coagulated with an aqueous calcium chloride solution, and the coagulated product was

20 filtered off and dried to obtain the dry powder of S-13. The conversion of glycidyl methacrylate was 98.5%, and the average particle size of the graft copolymer latex was 0.20 μm .

One piece of the S-13 film was put between

25 two pieces of polyethylene terephthalate film of 100 μm in thickness (trade name, LUMIRROR™; produced by Toray Industries, Inc.) and heat-pressed at 200°C for 10 minutes under a pressure of 10 kg/cm^2 to prepare a

1 three-layer sheet of which the middle layer was 20 μm
in thickness. A test piece of 10 mm in width was cut
out of this sheet, and a 180-degree peeling test was
carried out at 23°C and 0°C to measure the interlaminar
5 bond strength. The results are shown in Table 2.

Example 10

A composite rubber latex was obtained in the
same manner as in Example 1 except that 210 parts of
POS-1 obtained according to Example 1 was sampled, 143
10 parts of distilled water was added thereto, the amounts
of n-butyl acrylate, allyl methacrylate and tert-butyl
hydroperoxide added were 27 parts, 0.454 part and 0.065
part, respectively, and that the amounts of ferrous
sulfate, disodium ethylenediaminetetraacetate and
15 Rongalite™ were 0.00037 part, 0.00111 part and 0.089
part, respectively. To this rubber latex was dropwise
added a mixed solution of 10 parts of glycidyl meth-
acrylate and 0.024 part of tert-butyl hydroperoxide over
30 minutes. The reaction mixture was kept at an inner
20 temperature of 70°C for 4 hours to complete graft
polymerization onto the compound rubber. The conversion
of glycidyl methacrylate was 98.1%, and the average
particle size of the graft copolymer latex was 0.20 μm .
The resulting graft copolymer latex was coagulated
25 with an aqueous calcium chloride solution, and the
coagulated product was filtered off and dried to obtain
the dry powder of a polyorganosiloxane graft copolymer

1 (hereinafter referred to as S-14).

S-14 was evaluated in the same manner as in Example 9. The results are shown in Table 2.

Example 11

5 The dry powder of a polyorganosiloxane graft copolymer (hereinafter referred to as S-15) was obtained in the same manner as in Example 10 except that the amount of POS-1 sampled was 90 parts, the amount of distilled water added was 227 parts, the amounts of
10 n-butyl acrylate, allyl methacrylate and tert-butyl hydroperoxide added were 63 parts, 1.26 part and 0.151 part, respectively, and that the amounts of ferrous sulfate, disodium ethylenediaminetetraacetate and Rongalite™ were 0.00073 part, 0.0022 part and 0.18 part,
15 respectively. S-15 was evaluated in the same manner as in Example 9. The results are shown in Table 2. The conversion of glycidyl methacrylate was 97.2%, and the average particle size of the graft copolymer latex was 0.21 μm .

20 Example 12

Graft polymerization onto the compound rubber was carried out in the same manner as in Example 9 except that the amount of the compound rubber latex sampled was 360 parts, and a mixture of 5 parts of
25 glycidyl methacrylate and 5 parts of butyl acrylate was used in place of 10 parts of glycidyl methacrylate.

1 Thus, the latex of a polyorganosiloxane graft copolymer
(hereinafter referred to as S-16) was obtained. This
latex was coagulated with an aqueous calcium chloride
solution, and the coagulated product was filtered off
5 and dried to obtain the dry powder of S-16. The
conversion of glycidyl methacrylate and butyl acrylate
was 97.3%, and the average particle size of the graft
copolymer latex was 0.20 μm . S-16 was evaluated in
the same manner as in Example 9. The results are shown
10 in Table 2.

Example 13

The latex of a graft copolymer (hereinafter
referred to as S-17) was obtained in the same manner
as in Example 12 except that 5 parts of methyl meth-
15 acrylate was used in place of 5 parts of butyl acrylate.
This latex was coagulated, filtered off and dried to
obtain the dry powder of S-17. S-17 was evaluated in
the same manner as in Example 9. The results are
shown in Table 2. The conversion of glycidyl meth-
20 acrylate and methyl methacrylate was 97.8%, and the
average particle size of the graft copolymer latex was
0.21 μm .

Example 14

Graft polymerization onto the compound rubber
25 was carried out in the same manner as in Example 9 except
that the amount of the composite rubber latex sampled

1 was 240 parts, a mixture of 20 parts of glycidyl meth-
acrylate, 10 parts of butyl acrylate and 10 parts of
methyl methacrylate was used in place of 10 parts of
glycidyl methacrylate, and that the amount of tert-
5 butyl hydroperoxide added was 0.096 part. Thus, the
latex of a polyorganosiloxane graft copolymer (hereinafter
referred to as S-18) was obtained. This latex was
coagulated with an aqueous calcium chloride solution,
and the coagulated product was filtered off and dried
10 to obtain the dry powder of S-18. The conversion of
glycidyl methacrylate, butyl acrylate and methyl
methacrylate was 98.8%, and the average particle size
of the graft copolymer latex was 0.21 μm . S-18 was
evaluated in the same manner as in Example 9. The
15 results are shown in Table 2.

Example 15

The polyorganosiloxane graft copolymer (S-6)
obtained in Example 5 was evaluated in the same manner
as in Example 9. The results are shown in Table 2.

20 Example 16

The polyorganosiloxane graft copolymer (S-8)
obtained in Example 6 was evaluated in the same manner
as in Example 9. The results are shown in Table 2.

Comparative Example 5

25 Two hundred and ninety parts of the compound

1 rubber latex obtained in the same manner as in Example
1 was sampled, and a mixed solution of 10 parts of
methyl methacrylate and 0.024 part of tert-butyl hydro-
peroxide was added thereto. The resulting mixture was
5 kept at an inner temperature of 70°C for 4 hours to
carry out graft polymerization onto the composite rubber.
The conversion of methyl methacrylate was 98.8%, and
the average particle size of the graft copolymer latex
was 0.20 μm . The resulting latex was coagulated with
10 an aqueous calcium chloride solution, and the coagulated
product was filtered off and dried to obtain the dry
powder of a polyorganosiloxane graft copolymer (herein-
after referred to as S-19). This dry powder of S-19
was evaluated in the same manner as in Example 9. The
15 results are shown in Table 2.

Comparative Example 6

A three-layer laminated sheet was prepared
in the same manner as in Example 9 using an ethylene/
glycidyl methacrylate copolymer (trade name, Bondfast
20 ETM; produced by Sumitomo Chemical Co., Ltd.) The sheet
was then evaluated in the same manner as in Example 9.
The results are shown in Table 2.

Example 17

The latex of a graft copolymer (hereinafter
25 referred to as S-20) was obtained in the same manner as
in Example 13 except that 5 parts of glycidyl acrylate

1 was used in place of 5 parts of glycidyl methacrylate.
The conversion of glycidyl acrylate and methyl meth-
acrylate was 97.2%, and the average particle size of
the graft copolymer latex was 0.21 μm . This latex was
5 coagulated, filtered off and dried to obtain the dry
powder of S-20. S-20 was evaluated in the same manner
as in Example 9. The results are shown in Table 2.

Example 18

The latex of a graft copolymer (hereinafter
10 referred to as S-21) was obtained in the same manner as
in Example 13 except that 5 parts of diglycidyl itaconate
was used in place of 5 parts of glycidyl methacrylate.
The conversion of diglycidyl itaconate and methyl
methacrylate was 98.0%, and the average particle size
15 of the graft copolymer latex was 0.20 μm . This latex
was coagulated, filtered off and dried to obtain the
dry powder of S-21. S-21 was evaluated in the same
manner as in Example 9. The results are shown in Table 2.

Table 2

	Kind of adhesive	Bond strength at 23°C (g/cm)	Bond strength at 0°C (g/cm)
Example 9	S-13	890	840
Example 10	S-14	900	880
Example 11	S-15	850	800
Example 12	S-16	810	790
Example 13	S-17	820	780
Example 14	S-18	980	950
Example 15	S-6	1320	1230
Example 16	S-8	1160	1090
Comparative Example 5	S-19	50	40
Comparative Example 6	BF-E ¹⁾	960	320
Example 17	S-20	810	790
Example 18	S-21	960	910

1) Bondfast ETM

WHAT IS CLAIMED IS:

1. A polyorganosiloxane graft copolymer obtained by graft-polymerizing one or more kinds of monomer which have ethylenically unsaturated bond and contain at least an epoxy group-containing vinyl monomer onto a compound rubber in which a polyorganosiloxane rubber and a polyalkyl (meth)acrylate rubber have been inseparably united with each other, and in which the component derived from the epoxy group-containing vinyl monomer occupies a proportion of 1 to 30 wt.% of the whole graft copolymer.
2. The polyorganosiloxane graft copolymer according to Claim 1, wherein the compound rubber is obtained by polymerizing an alkyl (meth)acrylate, a crosslinking agent for polyalkyl (meth)acrylate rubber and a graft-linking agent for polyalkyl (meth)acrylate rubber in the presence of the polyorganosiloxane rubber obtained by emulsion-polymerizing organosiloxane, a crosslinking agent for polyorganosiloxane rubber and if necessary a graft-linking agent for polyorganosiloxane rubber.
3. The polyorganosiloxane graft copolymer according to Claim 1, wherein the polyorganosiloxane rubber comprises polydimethylsiloxane as the main component.
4. The polyorganosiloxane graft copolymer according to Claim 1, wherein the polyalkyl (meth)acrylate rubber comprises poly-n-butyl acrylate as the main component.
5. The polyorganosiloxane graft copolymer according to Claim 1, wherein the amounts of the polyorganosiloxane rubber component and the polyalkyl (meth)acrylate rubber

component constituting the compound rubber are 5 to 80 wt.% and 95 to 20 wt%, respectively.

6. The polyorganosiloxane graft copolymer according to Claim 2, wherein the crosslinking agent for the polyorganosiloxane rubber is a tetraalkoxysilane.

7. The polyorganosiloxane graft copolymer according to Claim 2, wherein the graft-linking agent for the polyorganosiloxane rubber is methacryloyloxysiloxane.

8. The polyorganosiloxane graft copolymer according to Claim 2, wherein both the crosslinking agent and graft-linking agent for the polyalkyl (meth)acrylate rubber are allyl methacrylate.

9. The polyorganosiloxane graft copolymer according to Claim 1, wherein the proportion of the component derived from one or more kinds of monomer which have an ethylenically unsaturated bond and contain at least an epoxy group-containing vinyl monomer to be graft-polymerized onto the compound rubber is 10 to 90 wt.% based on the whole polyorganosiloxane graft copolymer.

10. The polyorganosiloxane graft copolymer according to Claim 1, wherein the proportion of the component derived from one or more kinds of monomer which have an ethylenically unsaturated bond and contain at least an epoxy group-containing vinyl monomer to be graft-polymerized onto the compound rubber is 10 to 50 wt.% based on the whole polyorganosiloxane graft copolymer.

11. The polyorganosiloxane graft copolymer according to Claim 1, wherein the proportion of the component derived from the epoxy group-containing vinyl monomer is 2 to 30 wt.%.

12. The polyorganosiloxane graft copolymer according to any one of Claims 1 to 11, wherein the epoxy group-containing vinyl monomer is glycidyl methacrylate.

13. The polyorganosiloxane graft copolymer according to any one of Claims 1 to 11, wherein the epoxy group-containing vinyl monomer is glycidyl acrylate.