

SPECIFICATION

ACETAL COPOLYMER AND PROCESS FOR PRODUCING SAME

1 TECHNICAL FIELD

The present invention relates to a novel acetal copolymer and a process for producing it. More particularly, the present invention relates to an acetal
5 copolymer which comprises a polyacetal and a particulate crosslinked polymer other than a polyacetal which has a functional group and has an average particle size of 0.01-10 μm , said polyacetal and particulate crosslinked
10 group, and a process for producing an acetal copolymer which comprises homopolymerizing formaldehyde or trioxane or copolymerizing formaldehyde or trioxane with a cyclic ether in the presence of a polymer other than a polyacetal which has a functional group and has an
15 average dispersion particle size of 0.01-2,000 μm .

BACKGROUND TECHNIQUE

Recently, there has been a great demand for polyacetals as engineering plastics because of their superior mechanical characteristics, fatigue
20 characteristics and frictional wear characteristics. However, with diversification of uses and demand for enhancement of functions of polyacetals, properties

1 possessed by polyacetals cannot satisfy all of the requirements.

In order to improve this point, extensive research has been conducted on modification of
5 polyacetals, for example, a polymer alloying technique where a polyacetal and a resin other than a polyacetal are blended or a technique to modify the skeleton by introducing a component other than a polyacetal into the main chain of a polyacetal.

10 For example, as an example of the polymer alloying technique, EP-A-115373 discloses that a composition obtained by adding to a polyacetal an acrylic multi-phase interpolymer having a two-phase structure and having a particle size of 10-100 μ m is
15 excellent in impact resistance.

However, the acrylic multi-phase interpolymer disclosed in the above patent publication has a rigid thermoplastic phase as the outermost phase and since affinity of this outermost phase to a polyacetal is
20 insufficient, the composition cannot be said to be sufficient in high impact resistance required for engineering plastics. Further, the composition has the defect that impact resistance in a specific direction decreases significantly depending on processing conditions.

25 Specifically, impact resistance in a specific direction decreases when processing is conducted under conditions which apply orientation to the multi-phase interpolymer dispersed in the polyacetal in processing

1 such as injection molding, extrusion molding, and blow
molding. For example, in a weld portion which is formed
by joining molten resins to each other in a mold for
injection molded products, impact resistance in a
5 specific direction of the molded product, namely, weld
strength greatly decreases. This phenomenon occurs due
to the fact that the multi-phase interpolymer dispersed
in the polyacetal is not uniformly dispersed in all
portions of the molded product, but non-uniform un-
10 uniform dispersion such as agglomeration or orientation
occurs in the molded product.

Therefore, impact resistance of the composi-
tion disclosed in the above patent publication is non-
uniform and compositions having mechanical properties
15 excellent in isotropy cannot be obtained.

The mechanical properties excellent in
isotropy in the present invention mean mechanical
properties which show no reduction in tensile characte-
ristics and impact resistance in a specific direction in
20 any portion, especially a weld portion, of molded
products and having uniformity.

Examples of the technique to modify the
skeleton for solving the above problems are as shown
below.

25 For example, USP 4,535,127 discloses that
graft copolymers having a structure where a polyacetal
is grafted on elastomers such as modified ethylene-
propylene copolymer and modified styrene-butadiene
copolymer have high impact resistance.

1 Moreover, USP 4,535,127 discloses that A-B-A
triblock copolymers comprising polyacetal units (A) and
elastomer units (B) have excellent impact resistance.

 However, in these processes, normally,
5 copolymerization is carried out in a system where the
elastomer is completely dissolved in polymerization
solvents or the like. Therefore, the resulting acetal
copolymer just after being copolymerized is in a viscous
slurry state and there is the problem that filtration
10 and drying of the acetal copolymer are difficult and
when the processes are industrially carried out, it is
very difficult in the manufacturing technique to stably
mass-produce acetal copolymers. Besides, since this
problem becomes conspicuous with an increase in the
15 amount of elastomer introduced into the acetal
copolymer, acetal copolymers having a large introduction
amount of elastomer cannot be produced and this is a
serious obstacle in improving the impact resistance of
acetal copolymers.

20 Furthermore, according to the processes of the
above patent, acetal copolymers just after copolymeriza-
tion are a viscous slurry state and hence, in a short
time, the polymers stick to the wall of the polymeriza-
tion tank and smooth operation cannot be conducted.

25 This is a serious disadvantage.

DISCLOSURE OF THE INVENTION

 An object of the present invention is to solve
the problems in the conventional techniques and to

1 provide acetal copolymers having mechanical properties
excellent in isotropy while maintaining the excellent
mechanical characteristics, fatigue characteristics and
frictional wear characteristics possessed by polyacetals
5 and a process for producing acetal copolymers excellent
in production technique.

That is, as a result of intensive research
conducted by the inventors, it has been found that a
specific particulate crosslinked polymer functions as a
10 good molecular weight modifier and the resulting acetal
copolymers have mechanical properties excellent in
isotropy. It has further been found that the acetal
copolymers of the present invention can be produced
easily by using a specific particulate polymer as a
15 molecular weight modifier.

That is, the present invention relates to a
copolymer composed of polyacetal units and particulate
crosslinked polymer units which comprises a polyacetal
and a particulate crosslinked polymer other than a poly-
20 acetal which has a functional group selected from the
group consisting of a hydroxyl group, a carboxyl group,
an amino group, an amide group, an alkoxy group, an acid
anhydride group and an epoxy group and has an average
particle size of 0.01-10 μm , said polyacetal and partic-
25 ulate crosslinked polymer being reaction bonded through
said functional group, and which has a viscosity of 0.1-
10 (dl/g), and a process for producing an acetal copoly-
mer composed of polyacetal units and polymer units other

1 than polyacetals and having a viscosity of 0.1-10 (dl/g)
which comprises homopolymerizing formaldehyde or
trioxane or copolymerizing formaldehyde or trioxane with
a cyclic ether in the presence of a polymer other than a
5 polyacetal which has a functional group selected from
the group consisting of a hydroxyl group, a carboxyl
group, an amino group, an amide group, an alkoxy group,
an acid anhydride group, and an epoxy group and has an
average dispersion particle size of 0.01-2000 μ m, to
10 thereby allow the polyacetal and the polymer other than
a polyacetal to reaction bond to each other through the
above functional group.

Best Mode for Carrying Out the Invention

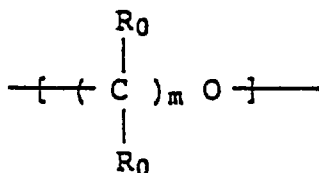
The acetal copolymers of the present invention
15 will be specifically explained.

The acetal copolymers of the present invention
are those which comprise polyacetal units and particu-
late crosslinked polymer units wherein a polyacetal and
a particulate crosslinked polymer having a functional
20 group selected from the group consisting of a hydroxyl
group, a carboxyl group, an amino group, an amide group,
an alkoxy group, an acid anhydride group, and an epoxy
group are reaction bonded through the functional group
and the copolymer has a structure of particulate cross-
25 linked polymer units being grafted on polyacetal units.

The polyacetal units in the present invention
include polyacetal homopolymer and polyacetal copolymer.
The polyacetal homopolymer is a polymer

- 1 comprising repeating oxymethylene units $\text{---} \text{CH}_2\text{O} \text{---}$.

The polyacetal copolymer is a polymer having a structure where oxyalkylene units:



- (wherein R_0 is selected from hydrogen, an alkyl group
5 and an aryl group and a plurality of R_0 may be identical or different and m is 2-6) are randomly inserted in a chain comprising oxymethylene units.

- The proportion of oxyalkylene units inserted in the polyoxymethylene copolymer is 0.05-50 mols, and
10 more preferably 0.1-20 mols, per 100 mols of oxymethylene units.

- The oxyalkylene units include, for example, oxyethylene units, oxypropylene units, oxytrimethylene units, oxytetramethylene units, oxybutylene units, and
15 oxyphenylethylene units.

Of these oxyalkylene units, oxyethylene units $\text{---} \text{CH}_2\text{O} \text{---}$ and oxytetraethylene units $\text{---} \text{CH}_2\text{O} \text{---}$ are especially preferred for improving the properties of the acetal copolymer.

- 20 The particulate crosslinked polymer unit which is another component of the acetal copolymer of the present invention is a particulate crosslinked polymer composed mainly of a copolymer of one or two or more vinyl monomers and a polyfunctional crosslinking

1 agent and is derived from a particulate crosslinked
polymer having a functional group selected from the
group consisting of a hydroxyl group, a carboxyl group,
an amino group, an amide group, an alkoxy group, an acid
5 anhydride group, and an epoxy group.

As the vinyl monomers, mention can be made of,
for example, aromatic compounds such as styrene, p-
methylstyrene, and α -methylstyrene; halogen compounds
such as vinyl chloride and vinylidene chloride; nitrile
10 compounds such as acrylonitrile and methacrylonitrile;
methacrylate esters such as methyl methacrylate, ethyl
methacrylate, propyl methacrylate, butyl methacrylate,
isobutyl methacrylate, and n-stearyl methacrylate;
acrylate esters such as methyl acrylate, ethyl acrylate,
15 n-butyl acrylate, and 2-ethylhexyl acrylate; vinyl
esters such as vinyl acetate and vinyl propionate, and
conjugated diene compounds such as butadiene and
isoprene.

These vinyl monomers can also be used in
20 combination of two or more.

These vinyl monomers are preferably acrylate
esters, methacrylate esters, conjugated diene compounds,
aromatic compounds and nitrile compounds.

More preferred are n-butyl acrylate, 2-
25 ethylhexyl acrylate, ethyl acrylate, isopropyl acrylate,
methyl methacrylate, ethyl methacrylate, propyl
methacrylate, isobutyl methacrylate, butadiene, styrene,
and acrylonitrile.

1 As the polyfunctional crosslinking agent,
there may be used crosslinking agents which are
generally used, such as divinyl compounds, diallyl
compounds, and dimethacryl compounds and preferred are
5 ethyl diacrylate, n-butyl diacrylate, and diethylene
glycol diacrylate. The proportion of the polyfunctional
crosslinking agent is preferably 0.1-20% by weight, and
more preferably, 0.1-5.0% by weight based on total
weight of the particulate crosslinked polymer.

10 The particulate crosslinked polymer having a
functional group is a particulate polymer having an
average particle size of 0.01-10 μm which is obtained by
copolymerizing one or more vinyl monomers constituting
the particulate crosslinked polymer unit, a polyfunc-
15 tional crosslinking agent, and one or more graft-co-
polymerizable vinyl monomers having a functional group
selected from the group consisting of a hydroxyl group,
a carboxyl group, an amino group, an amide group, an
alkoxy group, an acid anhydride group, and an epoxy
20 group.

 The functional group of the particulate cross-
linked polymer is derived from the functional group of
the above graft-copolymerizable vinyl monomer and the
acetal copolymer of the present invention comprising the
25 polyacetal and the particulate crosslinked polymer are
reaction bonded through the functional group of the
graft-copolymerizable vinyl monomer.

1 The graft-copolymerizable monomers having a functional group can be classified into the following seven groups.

 The first group includes graft-copolymerizable
5 vinyl monomers having a hydroxyl group such as, for example, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, p-hydroxystyrene, allyl alcohol, and vinyl alcohol.

 The second group includes graft-copolymeriz-
10 able vinyl monomers having a carboxyl group such as, for example, acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, and tetrahydrophthalic acid.

 The third group includes graft-copolymerizable
15 vinyl monomers having an amino group such as, for example, m-aminostyrene and p-dimethylaminostyrene.

 The fourth group includes graft-copolymeriz-
able vinyl monomers having an amide group such as, for example, acrylamide and methacrylamide.

20 The fifth group includes graft-copolymerizable monomers having an alkoxy group such as, for example, methoxyvinyl, butoxyvinyl, p-methoxystyrene, and 2-methoxyethyl methacrylate.

 The sixth group includes graft-copolymerizable
25 vinyl monomers having an acid anhydride group such as, for example, maleic anhydride, citraconic anhydride, itaconic anhydride and tetrahydrophthalic anhydride.

 The seventh group includes graft-copolymeriz-

1 able vinyl monomers having an epoxy group such as, for
example, p-glycidyl α -methylstyrene, glycidyl methacry-
late, glycidylethyl acrylate, glycidylethyl methacry-
late, and glycidylvinyl.

5 These graft-copolymerizable vinyl monomers can
also be used simultaneously in a combination of two or
more.

 Furthermore, introduction of a functional
group into the particulate crosslinked polymer can also
10 be carried out by reacting a reactive group contained in
the particulate crosslinked polymer with a reactive
group of a compound having a functional group and a re-
active group in combination. Alternatively, the partic-
ulate crosslinked polymer can also be synthesized by
15 modifying a functional group introduced into a particu-
late crosslinked polymer by means of hydrolysis or the
like.

 Graft-copolymerizable vinyl monomers are
preferably graft-copolymerizable vinyl monomers having a
20 hydroxyl group from the point of stability of reaction
bonding between the polyacetal and the particulate
crosslinked polymer.

 The proportion of the graft-copolymerizable
vinyl monomer is preferably 0.05-30% by weight based on
25 the total weight of the particulate crosslinked polymer.
If it is less than 0.05% by weight, reaction bonding
between the polyacetal and the particulate crosslinked
polymer is difficult and, if it is more than 30% by

1 weight, mechanical properties of the resulting acetal
copolymer greatly deteriorate. A more preferred range
is 0.1-20% by weight.

The particulate crosslinked polymer is a
5 polymer which is particulate in its primary form and has
an average particle size of 0.01-10 μm . The primary
form is a form which constitutes a minimum unit of
particulate crosslinked polymer and is normally handled
as an agglomerate of particles in this primary form.

10 If the average particle size of the particu-
late crosslinked polymer is less than 0.01 μm , excellent
properties such as impact resistance and weathering
resistance possessed by the particulate crosslinked
polymer cannot be imparted to acetal copolymer and if it
15 is more than 10 μm , mechanical properties excellent in
isotropy referred to in the present invention cannot be
imparted to the acetal copolymer.

The average particle size of the particulate
crosslinked polymer is more preferably within the range
20 of 0.1-1 μm .

The particulate crosslinked polymer preferably
has a narrow breadth of particle size distribution.
When particle size distribution is wide, the mechanical
properties excellent in isotropy referred to in the
25 present invention cannot be imparted to the resulting
acetal copolymer.

The particle size distribution of the particu-
late crosslinked polymer is more preferably within the

1 range of 0.01-20 μ m.

The viscosity of the acetal copolymer of the present invention must be within the range of 0.1-10 (dl/g).

5 The viscosity used herein is one measured in a mixed solvent of 50% by weight of p-chlorophenol and 50% by weight of tetrachloroethane at 60°C by a usual Ostwald viscometer. Specifically, 25 mg of a sample (polymer) to be measured is dissolved in 5 ml of the
10 above mixed solvent and the time (T_1) required for the solution to pass between marked lines of the viscosity tube is measured at 60°C. Similarly, measurement is conducted with only the mixed solvent and the time required is referred to as T_2 . The viscosity in the
15 present invention is obtained by the following calculation formula.

$$\text{Viscosity} = \frac{T_1 - T_2}{T_2} \times 2 \text{ (dl/g)}$$

If the viscosity of the acetal copolymer is less than 0.1 (dl/g), mechanical properties of the acetal copolymer deteriorate to lose practicality. If
20 the viscosity is more than 10 (dl/g), processability of the acetal copolymer deteriorates considerably and in this case, too, the acetal copolymer lacks practicality.

The viscosity of the acetal copolymer is more preferably 0.5-5 (dl/g).

25 The particulate crosslinked polymer units of the present invention may have a multi-phase structure

1 of two or more phases comprising repeating soft and hard
phases. The "soft phase" herein means a phase compris-
ing a polymer softer than the polymer constituting the
hard phase and the "hard phase" here means a phase
5 comprising a polymer harder than the polymer constitut-
ing the soft phase.

The glass transition temperature (hereinafter
referred to as "Tg") of the polymer constituting the
soft phase is preferably lower than 25°C and more
10 preferably lower than 0°C. The Tg of the polymer
constituting the hard phase is preferably 25°C or
higher, more preferably 50°C or higher.

Preferably, the polymer has a soft phase
comprising an acrylate ester or a conjugated diene
15 compound and a hard phase comprising a methacrylate
ester, an aromatic compound or a nitrile compound. More
preferably, the soft phase comprises n-butyl acrylate,
2-ethylhexyl acrylate, ethyl acrylate, isopropyl
acrylate, butadiene, or styrene-butadiene and the hard
20 phase comprises methyl methacrylate, ethyl methacrylate,
propyl methacrylate, isobutyl methacrylate, styrene, or
acrylonitrile.

When the particulate crosslinked polymer unit
has a multi-phase structure, the particulate crosslinked
25 polymer unit preferably has a two-phase structure.

When the particulate crosslinked polymer has a
multi-phase structure, the boundary between respective
phases may be an unclear and vague boundary. For

1 example, in the case of a particulate crosslinked
polymer of a two-phase structure which has a hard phase
outside a soft phase, the boundary between the soft and
hard phases may be a vague boundary which has a gradual
5 variation in composition from the composition of the
polymer constituting the soft phase to the composition
of the polymer constituting the hard phase. In this
case, when a part of the polymer constituting the hard
phase enters into the soft phase and forms fine and many
10 domains, the particulate crosslinked polymer unit can
also be said to have the multi-phase structure of the
present invention.

When the particulate crosslinked polymer unit
has a multi-phase structure, it is preferred to use the
15 above-mentioned polyfunctional crosslinking agent and
the following polyfunctional grafting agent in
combination.

The polyfunctional grafting agent includes
polyfunctional monomers having functional groups dif-
20 ferent in reaction rate such as, for example, allyl
esters of acrylic acid, methacrylic acid, maleic acid
and fumaric acid. Allyl acrylate and allyl methacrylate
are preferred. The proportion of the polyfunctional
grafting agent is preferably 0.1-5.0% by weight, and
25 more preferably 0.1-2.5% by weight, based on the total
weight of the polymer constituting the phase which is
the base for grafting.

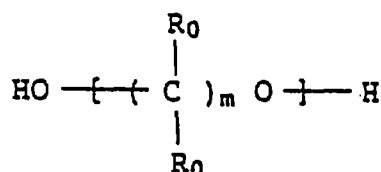
The proportion of the particulate crosslinked

1 polymer contained in the acetal copolymer of the present
invention is preferably 1.0-90% by weight based on the
total weight of acetal copolymer. If the proportion of
particulate crosslinked polymer is less than 1.0% by
5 weight, the excellent characteristics such as impact
resistance and weathering resistance possessed by the
particulate crosslinked polymer cannot be imparted to
the acetal copolymer and if it is more than 90% by
weight, the excellent mechanical properties and fric-
10 tional wear characteristics possessed by the polyacetal
cannot be imparted to the acetal copolymer.

The proportion of the particulate crosslinked
polymer is more preferably 5.0-70% by weight.

The proportion of the particulate crosslinked
15 polymer in the acetal copolymer of the present invention
or the structure of the acetal copolymer (presence or
absence of reaction bonding between the polyacetal and
the particulate crosslinked polymer) can be confirmed by
the following method.

20 That is, when the acetal copolymer is hydro-
lyzed in an acidic aqueous solution, the portion com-
prising the repeating oxymethylene units is converted to
formaldehyde and the portion of oxyalkylene unit
inserted into the polyacetal copolymer is converted to
25 an alkylene glycol of the following formula:



1 (wherein R_0 is selected from hydrogen, an alkyl group
and aryl group and a plurality of R_0 may be identical or
different and $m=2-6$).

The formaldehyde and alkylene glycol are
5 analyzed and amounts thereof are determined by means
such as gas chromatography and liquid chromatography.

The particulate crosslinked polymer units
contained in the acetal copolymer become the particulate
crosslinked polymer having the functional group
10 mentioned above since the bond between the polyacetal
units and particulate crosslinked polymer units is cut.
This particulate crosslinked polymer is precipitated
from aqueous solution. Analysis and determination of
the amount of the precipitated particulate crosslinked
15 polymer are conducted by a usual polymer analysis
method.

It is preferred to use a suitable particulate
crosslinked polymer depending on the required character-
istics of the acetal copolymer of the present invention.

20 For example, when impact resistance is
imparted to the acetal copolymer, the particulate
crosslinked polymer units preferably comprise a polymer
having a T_g of lower than 25°C , and preferably lower
than 0°C . Alternatively, preferred are particulate
25 crosslinked polymer units of two-phase structure having
a hard phase outside a soft phase and having a higher
proportion of the soft phase, the T_g of the polymer
constituting the soft phase being preferably lower than

1 25°C, and more preferably lower than 0°C.

Furthermore, when weathering resistance is imparted to the acetal copolymer, it is preferred to use particulate crosslinked polymer units comprising an
5 acrylate ester or methacrylate ester which is superior in weathering resistance.

Besides, when coating and printing characteristics are imparted to the acetal copolymer, it is preferred to use particulate crosslinked polymer unit
10 comprising compounds low in solvent resistance and high in polarity such as aromatic compounds, nitrile compounds, methacrylate esters, and acrylate esters. More preferred is to use particulate crosslinked polymer units comprising styrene, acrylonitrile, methyl
15 methacrylate, isobutyl methacrylate or methyl acrylate.

Next, the process for producing the acetal copolymer of the present invention will be explained.

The acetal copolymer of the present invention can be produced by homopolymerizing formaldehyde or
20 trioxane or copolymerizing formaldehyde or trioxane with a cyclic ether in the presence of a particulate crosslinked polymer other than a polyacetal which has a functional group selected from the group consisting of a hydroxyl group, a carboxyl group, an amino group, an
25 amide group, an alkoxy group, an acid anhydride group, and an epoxy group and has an average dispersion particle size of 0.01-2000 μm .

1 The particulate crosslinked polymer used in
the present invention can be produced by the following
process.

5 The particulate crosslinked polymer of the
present invention is a polymer other than a polyacetal
which has a functional group selected from the group
consisting of a hydroxyl group, a carboxyl group, an
amino group, an amide group, an alkoxy group, an acid
anhydride group and an epoxy group and has an average
10 particle size of 0.01-10 μm .

 The particulate crosslinked polymer can be
produced by a customary emulsion polymerization
technique using a vinyl monomer mentioned below, a
graft-copolymerizable vinyl monomer having a functional
15 group selected from the group consisting of a hydroxyl
group, a carboxyl group, an amino group, an amide group,
an alkoxy group, an acid anhydride group and an epoxy
group, and a polyfunctional crosslinking agent for giv-
ing a proper crosslinking degree. When the particulate
20 crosslinked polymer should have a multi-phase structure,
a polyfunctional grafting agent for chemical bonding of
respective phases is used in addition to the above vinyl
monomer, graft-copolymerizable vinyl monomer and poly-
functional crosslinking agent.

25 As usable vinyl monomers, mention can be made
of, for example, aromatic compounds such as styrene, p-
methylstyrene, and α -methylstyrene; halogen compounds
such as vinyl chloride and vinylidene chloride; nitrile

1 compounds such as acrylonitrile and methacrylonitrile:
methacrylate esters such as methyl methacrylate, ethyl
methacrylate, propyl methacrylate, butyl methacrylate,
isobutyl methacrylate, and n-stearyl methacrylate;
5 acrylate esters such as methyl acrylate, ethyl acrylate,
n-butyl acrylate, and 2-ethylhexyl acrylate; vinyl
esters such as vinyl acetate and vinyl propionate; and
conjugated diene compounds such as butadiene and
isoprene.

10 These vinyl monomers can also be used simul-
taneously in a combination of two or more.

 These vinyl monomers are preferably acrylate
esters, methacrylate esters, conjugated diene compounds,
aromatic compounds and nitrile compounds.

15 More preferred are n-butyl acrylate, 2-
ethylhexyl acrylate, ethyl acrylate, isopropyl acrylate,
methyl methacrylate, ethyl methacrylate, propyl
methacrylate, isobutyl methacrylate, butadiene, styrene,
and acrylonitrile.

20 The graft-copolymerizable monomers having a
functional group can be classified into the following
seven groups.

 The first group includes graft-copolymerizable
vinyl monomers having a hydroxyl group such as, for
25 example, 2-hydroxyethyl methacrylate, 2-hydroxyethyl
acrylate, p-hydroxystyrene, allyl alcohol, and vinyl
alcohol.

1 The second group includes graft-copolymeriz-
able vinyl monomers having a carboxyl group such as, for
example, acrylic acid, methacrylic acid, maleic acid,
fumaric acid, itaconic acid, citraconic acid, and
5 tetrahydrophthalic acid.

 The third group includes graft-copolymerizable
vinyl monomers having an amino group such as, for
example, m-aminostyrene and p-dimethylaminostyrene.

 The fourth group includes graft-copolymeriz-
10 able vinyl monomers having an amide group such as, for
example, acrylamide and methacrylamide.

 The fifth group includes graft-copolymerizable
monomers having an alkoxy group such as, for example,
methoxyvinyl, butoxyvinyl, p-methoxystyrene, and 2-
15 methoxyethyl methacrylate.

 The sixth group includes graft-copolymerizable
vinyl monomers having an acid anhydride group such as,
for example, maleic anhydride, citraconic anhydride,
itaconic anhydride and tetrahydrophthalic anhydride.

20 The seventh group includes graft-copolymeriz-
able vinyl monomers having an epoxy group such as, for
example, p-glycidyl α -methylstyrene, glycidyl
methacrylate, glycidylethyl acrylate, glycidylethyl
methacrylate, and glycidylvinyl.

25 These graft-copolymerizable vinyl monomers can
also be used simultaneously in a combination of two or
more.

 Furthermore, introduction of a functional

1 group into the particulate crosslinked polymer can also
be carried out by reacting a reactive group contained in
the particulate crosslinked polymer with a reactive
group of a compound having a functional group and a
5 reactive group in combination. Alternatively, the
particulate crosslinked polymer having a functional
group can also be synthesized by modifying a functional
group introduced into a particulate crosslinked polymer
by means of hydrolysis or the like.

10 When the polyacetal and the particulate
crosslinked polymer are reaction bonded to each other,
the reaction bonding is carried out through the graft-
copolymerizable monomer.

 The graft-copolymerizable monomer, namely, the
15 functional group which the particulate crosslinked
polymer has is preferably a graft-copolymerizable
monomer having a hydroxyl group, considering the
reaction rate for the functioning of the particulate
crosslinked polymer as a molecular weight modifier
20 during synthesis of the polyacetal.

 The proportion of the graft-copolymerizable
vinyl monomer is preferably 0.05-30% by weight based on
the total weight of the particulate crosslinked polymer.
If it is less than 0.05% by weight, reaction bonding
25 between the polyacetal and the particulate crosslinked
polymer is difficult and if it is more than 30% by
weight, mechanical properties of the resulting acetal
copolymer greatly deteriorate.

1 A more preferred range is 0.1-20% by weight.

 Furthermore, the molecular weight of the
polyacetal unit which constitutes the resulting acetal
copolymer is determined depending on the proportion of
5 graft-copolymerizable vinyl monomer, namely, proportion
of functional groups possessed by the particulate
crosslinked polymer. Therefore, it is preferred to
determine the proportion of the graft-copolymerizable
vinyl monomer depending on the molecular weight of the
10 desired polyacetal unit.

 As the polyfunctional crosslinking agent,
there may be used crosslinking agents usually employed
such as divinyl compounds, diallyl compounds, diacryl
compounds, and dimethacryl compounds. Preferred are
15 ethyl diacrylate, n-butyl diacrylate, and diethylene
glycol diacrylate. The proportion of the polyfunctional
crosslinking agent is preferably 0.1-20% by weight, and
more preferably 0.1-5.0% by weight, based on the total
weight of the particulate crosslinked polymer.

20 The polyfunctional grafting agent includes
polyfunctional monomers having functional groups
different in reaction rate, for example, allyl esters of
acrylic acid, methacrylic acid, maleic acid, and fumaric
acid and preferred are allyl acrylate and allyl
25 methacrylate. The proportion of the polyfunctional
grafting agent is preferably 0.1-5.0% by weight, and
more preferably 0.1-2.5% by weight.

1 The particulate crosslinked polymer of the
present invention can be produced, for example, by the
following general emulsion polymerization method.

 As an example, the production of a particulate
5 crosslinked polymer having a two-phase structure having
a hard phase outside a soft phase will be shown.

 Vinyl monomer, polyfunctional crosslinking
agent, polyfunctional grafting agent and polymerization
initiator necessary for formation of the soft phase are
10 added to water containing additives such as an
emulsifier necessary for emulsion polymerization and
polymerization is carried out with stirring.

 As the emulsifier, there may be used
alkylsulfosuccinate salts such as sodium dioctyl-
15 sulfosuccinate, alkylaromatic sulfonate salts such as
sodium dodecylbenzenesulfonate, and the like.

 As the polymerization initiator, there may be
used peroxides such as diisopropylbenzene hydroperoxide
and benzoyl peroxide; azo compounds such as azo-
20 bisisobutyronitrile; and the like.

 When the polymerization reaction for forming
the soft phase has been completed, then monomers for
forming the hard phase are additionally added. In this
case, if necessary, a polymerization initiator and
25 emulsifier may be additionally added.

 For producing a particulate crosslinked
polymer having a large average particle size, it is
preferred to repeat several times the procedure of

1 removing unnecessary emulsifier, polymerization
initiator, and unreacted monomers in the polymerization
system and thereafter further adding proper amounts of
monomers, emulsifier and polymerization initiator.

5 Emulsion polymerization is usually carried out
at 50-90°C.

The particulate crosslinked polymer obtained
by the above emulsion polymerization can be decomposed
with water while maintaining the shape of the particles
10 by customary means such as salting-out, freeze-thawing
and spray drying. The salting-out is carried out using
a solution of electrolytes such as aluminum chloride and
sodium chloride and the precipitate is filtered off.
The precipitate is further subjected to washing and
15 drying to obtain the particulate crosslinked polymer of
the present invention.

For inhibiting a reduction in the heat
stability of the resulting acetal copolymer, it is pre-
ferred to remove a catalyst such as peroxide used in the
20 emulsion polymerization and impurities as much as pos-
sible from the particulate crosslinked polymer prior to
producing the acetal copolymer of the present invention.

Next, the process for producing the acetal
copolymer of the present invention using the thus
25 obtained particulate crosslinked polymer will be shown.

For easy production of the acetal copolymer
which is a feature of the present invention, it is
necessary to allow the particulate crosslinked polymer

to be present as fine particles of 0.01-2,000 μm in
1 average dispersion particle size in the polymerization
system.

The words "in the polymerization system" mean
"in the polymerization system where formaldehyde or
5 trioxane is homopolymerized or formaldehyde or trioxane
is copolymerized with a cyclic ether".

The "average dispersion particle size" means
"average diameter of individual particles or
agglomerates of particulate crosslinked polymer present
10 in the polymerization system". That is, the average
dispersion particle size includes the diameters of
agglomerates of a portion of particulate crosslinked
polymer having an average particle size of 0.01-10 μm .

If the average dispersion particle size is
15 less than 0.01 μm , the excellent properties such as
impact resistance and weathering resistance possessed by
the particulate crosslinked polymer cannot be imparted
to the acetal copolymer. If it is more than 2,000 μm ,
the function of the particulate crosslinked polymer as a
20 molecular weight modifier during synthesis of the acetal
copolymer is lowered.

The average dispersion particle size of the
particulate crosslinked polymer is more preferably 0.1-
1,000 μm .

25 The particulate crosslinked polymer preferably
has a narrow breadth of dispersion particle size. When
the breadth of dispersion particle size is broad, an
acetal copolymer having mechanical properties excellent
in isotropy cannot be obtained.

1 The distribution of dispersion particle size
of the particulate crosslinked polymer is more
preferably 0.01-1,000 μm .

 Desirably, the particulate crosslinked polymer
5 is purified by washing, adsorption, drying and the like
before polymerization. Furthermore, the particulate
crosslinked polymer can also be supplied in an admixture
of two or more for polymerization.

 It is preferred that particles of the particu-
10 late crosslinked polymer are swollen to such extent that
the shape of the particles is not greatly destroyed in
the polymerization system. This is for enhancing the
function of the particulate crosslinked polymer having a
functional group as a molecular weight modifier. On the
15 other hand, if particles of the particulate crosslinked
polymer are swollen too much in the polymerization
system and the shape of the particles is lost or the
particles are in a completely dissolved state, the
resulting acetal copolymer is in the form of a viscous
20 slurry. In this case, filtration and drying of the
acetal copolymer are difficult and the object of the
present invention to produce an acetal copolymer easily
with respect to the production technique cannot be
attained.

25 Formaldehyde or trioxane is used in the
homopolymerization in the present invention. Formalde-
hyde or trioxane and cyclic ethers are used in the
copolymerization.

1 The cyclic ethers used in the copolymerization
include, for example, ethylene oxide, propylene oxide,
butylene oxide, epichlorohydrin, styrene oxide, oxetane,
3,3-bis(chloromethyl)oxetane, tetrahydrofuran, oxevan,
5 ethylene glycol formal, propylene glycol formal,
diethylene glycol formal, triethylene glycol formal,
1,4-butanediol formal, 1,5-pentanediol formal, and 1,6-
hexanediol formal. Of these cyclic ethers, especially
preferred are ethylene oxide, ethylene glycol formal,
10 diethylene glycol formal and 1,4-butanediol formal.

 The proportion of the cyclic ether is
preferably 0.03-100 parts by weight, and more preferably
0.1-50 parts by weight, per 100 parts by weight of
formaldehyde or trioxane.

15 Generally, cationic polymerization catalysts
or anionic polymerization catalysts are used for the
homopolymerization and copolymerization according to the
present invention.

 The cationic polymerization catalysts include,
20 for example, so-called Friedel-Crafts type compounds
such as tin tetrachloride, tin tetrabromide, titanium
tetrachloride, aluminum trichloride, zinc chloride,
vanadium trichloride, antimony pentafluoride, boron
trifluoride, boron trifluoride diethyl etherate, boron
25 trifluoride acetic anhydrate, and boron trifluoride
coordination compounds, e.g., a boron trifluoride
triethylamine complex compound; inorganic acids and
organic acids such as perchloric acid, acetyl

1 perchlorate, hydroxyacetic acid, trichloroacetic acid,
and p-toluenesulfonic acid; composite salt compounds
such as triethyloxonium tetrafluoroborate, triphenyl-
methyl hexafluoroantimonate, allyldiazonium hexafluoro-
5 phosphate, and allyldiazonium tetrafluoroborate; and
alkyl metals such as diethylzinc, triethylammonium and
diethylaluminum chloride.

Anionic polymerization catalysts include, for
example, alkali metals such as sodium and potassium;
10 alkali metal complex compounds such as sodium-
naphthalene and potassium-anthracene; alkali metal
hydrides such as sodium hydride; alkaline earth metal
hydrides such as calcium hydride; alkali metal alkoxides
such as sodium methoxide, potassium t-butoxide, and
15 potassium octoxide; alkali metal salts of carboxylic
acids such as sodium caproate and potassium stearate;
alkaline earth metal salts of carboxylic acids such as
magnesium caproate and calcium stearate; amines such as
n-butylamine, dibutylamine, distearylamine, tri-
20 octylamine, and pyridine; quaternary ammonium salts such
as ammonium stearate, tetrabutylammonium methoxide,
tetrabutylammonium octanoate, dimethyldistearylammmonium
acetate, trimethylbenzylammonium acetate, and tri-
methylbenzylammonium methoxide; phosphonium salts such
25 as tetramethylphosphonium propionate, trimethyl-
benzylphosphonium ethoxide and tetrabutylphosphonium
stearate; tetravalent organotin compounds such as
tributyltin chloride, diethyltin dilaurate,

1 dibutyltin dimethoxide, dibutyltin dilaurate, dioctyltin
dilaurate; and tributyltin laurate; alkyl metals such as
n-butyllithium and ethylmagnesium bromide; and organic
chelate compounds such as trisacetylacetonecobalt.

5 These cationic polymerization catalysts and
anionic polymerization catalysts are used normally in an
amount of 0.0005-5 parts by weight per 100 parts by
weight of formaldehyde or trioxane.

 The homopolymerization or copolymerization is
10 carried out in the absence of a solvent or in an organic
medium.

 The organic medium usable in the present
invention includes, for example, aliphatic hydrocarbons
such as n-pentane, n-hexane, n-heptane, n-octane,
15 cyclohexane, and cyclopentane; aromatic hydrocarbons
such as benzene, toluene and xylene; halogenated
aliphatic hydrocarbons such as methylene chloride,
chloroform, carbon tetrachloride, ethylene chloride, and
trichloroethylene; and halogenated aromatic hydrocarbons
20 such as chlorobenzene and o-dichlorobenzene. These
organic media may be used singly or in an admixture of
two or more.

 It is preferred to use these organic media in
such combination that properly swell the particulate
25 crosslinked polymer dispersed in the polymerization
system.

 Polymerization temperature is usually set in
the range of -20 - 230°C, but is more preferably 20-

1 210°C in the case of not using a solvent and, in the
case of using an organic medium, is more preferably -10
- 120°C.

Polymerization time is not critical, but is
5 set within the range of 5 seconds - 300 minutes.

After lapse of a given time, a terminator is
added to the reaction system or the polymer is separated
from the medium, thereby to complete polymerization.
Usually, the resulting polymer is stabilized by
10 eliminating unstable terminals by hydrolysis or by
capping the unstable terminals by esterification or the
like. The stabilized acetal copolymer to which a
stabilizer is added is put into practical use.

In the production of the acetal copolymer of
15 the present invention, other polyacetals excellent in
isotropy can also be obtained easily with respect to the
production technique by using polymers other than the
above-mentioned particulate crosslinked polymer and
other than the polyacetal. The "other polyacetals" here
20 means acetal copolymers obtained by using polymers other
than a polyacetal in place of the above particulate
crosslinked polymer.

That is, another object of the present
invention is to provide a process for producing an
25 acetal copolymer composed of polyacetal units and
polymer units other than polyacetal which comprises a
polyacetal and a polymer other than a polyacetal which
are reaction bonded through a functional group mentioned

1 below and which has a viscosity of 0.1-10 (dl/g),
characterized by homopolymerizing formaldehyde or
trioxane or copolymerizing formaldehyde or trioxane with
a cyclic ether in the presence of a polymer other than a
5 polyacetal which has a functional group selected from
the group consisting of a hydroxyl group, a carboxyl
group, an amino group, an amide group, an alkoxy group,
an acid anhydride group, and an epoxy group and has an
average dispersion particle size of 0.01-2000 μ m.

10 Polymers other than a polyacetal and other
than the particulate crosslinked polymer (hereinafter
referred to as "other polymers") in the present inven-
tion can be classified into the following two groups.

 The first group includes polymers (hereinafter
15 referred to as "polymer ①") having at a terminal at
least one functional group selected from the group
consisting of a hydroxyl group, a carboxyl group, an
amino group, an amide group, an alkoxy group, an acid
anhydride group and an epoxy group. The second group
20 includes polymers (hereinafter referred to as "polymer
②") having at least one of the above functional groups
in the main chain.

 When the polyacetal is referred to as A and
the other polymer is referred to as B and when polymer
25 ① has a functional group at one terminal thereof, A-B
diblock copolymers can be obtained and when polymer ①
has functional groups at both terminals, A-B-A triblock
copolymers can be obtained. Furthermore, when the other

1 polymer is polymer ②, acetal graft copolymers having B as a backbone polymer and A as a branch polymer can be obtained.

Compounds of polymer ① include, for example,
5 rigid polymers such as polyamides (nylon-6, -66, -11, -12, etc.), polyethylene terephthalate, polybutylene terephthalate, polycarbonate, polyphenylene ether, polyarylate, and polyphenylene sulfide and soft polymers such as thermoplastic elastomers of the polyester type,
10 polyurethane type, polyamide type and polystyrene type.

Compounds of polymer ② include, for example, compounds shown below and compounds obtained by modifying the compounds shown below using graft-copolymerizable vinyl monomers as referred to hereinbefore in the
15 presence or absence of a peroxide by an extruder or the like (hereinafter referred to as modified polymer ②).

That modified polymer ② has been modified with a graft-copolymerizable vinyl monomer can be easily confirmed by general analysing techniques such
20 as IR.

Polymers ② or compounds usable for production of modified polymers ② include, for example, rigid polymers such as AAS resin, AES resin, AS resin, ABS resin, ethylene-vinyl chloride copolymer, high-density
25 polyethylene, low-density polyethylene, polypropylene, ultra-high molecular weight polyethylene, polyvinyl alcohol, and polyvinyl ether and soft polymers such as ethylene-propylene copolymer, ethylene-propylene-diene

1 copolymer, styrene-diene copolymer, hydrogenated
styrene-diene copolymer, isobutylene-maleic anhydride
copolymer, ethylene-vinyl acetate copolymer, poly-
butadiene, polyisoprene, and acetonitrile-butadiene
5 copolymer.

The functional group possessed by the other
polymer is preferably a hydroxyl group in view of
stability of the acetal copolymer as in the case of the
particulate crosslinked polymer.

10 When the other polymer is modified polymer ②,
the proportion of graft-copolymerizable monomer used for
preparation of the modified polymer ② is preferably
0.05-30% by weight, and more preferably 0.1-20% by
weight.

15 For easy production of the acetal copolymer
with respect to the production technique which is a
feature of the present invention, it is necessary to
allow the other polymer to be present as fine particles
of 0.01-2,000 μm in average dispersion particle size in
20 the polymerization system of the present invention as in
the case of the particulate crosslinked polymer. The
other polymer can be made into fine particles by grind-
ing it using a customary grinder or the other polymer in
the form of particles present in the production process
25 of the other polymer can be used as it is.

A more preferred breadth of distribution of
average dispersion particle size of the other polymer is
0.1-1,000 μm .

1 A narrow distribution of dispersion particle
size of the other polymer in the polymerization system
is preferred and more preferred is 0.01-3,000 μm .

5 Furthermore, it is preferred that particles of
the other polymer are swollen to such an extent in the
polymerization system that the shape of the particles is
not greatly damaged.

10 On the other hand, if the particles of the
other polymer are swollen too much and the shape of the
particles is lost or they are completely dissolved in
the polymerization system, the resulting acetal
copolymer is in the state of a viscous slurry. Thus,
filtration and drying of the acetal copolymer are
difficult and the object of the present invention to
15 produce the acetal copolymer easily with respect to
production technique cannot be attained.

20 The proportion of the other polymer in the
acetal copolymer obtained in the present invention is
preferably 1.0-90% by weight, and more preferably 5.0-
70% by weight, based on the total weight of the acetal
copolymer.

25 As the other polymers used in the present
invention, there may be used appropriate polymers
depending on the characteristics required for the
resulting acetal copolymer.

For example, when impact resistance is to be
imparted to acetal copolymer, the other polymer is
preferably a soft polymer and more preferably, a polymer
② such as ethylene-propylene copolymer, ethylene-

1 propylene-diene copolymer, styrene-diene copolymer, and
hydrogenated styrene-diene copolymer. Dienes
copolymerized with ethylene-propylene copolymer here are
preferably dicyclopentadiene, ethylidenenorbornene,
5 methylenenorbornene, and 1,4-hexadiene. Dienes
copolymerized with styrene are preferably butadiene,
isoprene and cyclopentadiene.

When sliding characteristic is the imparted to
the acetal copolymer, the other polymers are preferably
10 polymers ② such as high-density polyethylene, low-
density polyethylene, ultra-high molecular weight
polyethylene and ethylene-propylene copolymer.

When weathering resistance and coating and
printing characteristics are to be imparted to the
15 polyacetal copolymer, the other polymers are preferably
polymers ② such as AAS resin, AES resin, AS resin, and
ABS resin.

Features of the process for producing the
acetal copolymer of the present invention can be
20 summarized as follows.

(1) The acetal copolymer just after copoly-
merization is in the form of particles and there are no
problems in production technique such as filtration and
drying and the process can be industrially practised.

25 (2) The polymer other than the polyacetal is
in the form of fine particles in the polymerization
system and so it functions as a molecular weight
modifier at a high rate and an acetal copolymer having
excellent properties can be obtained.

1 (3) Because of easiness in the production
technique (related to (1)), production of an acetal
copolymer containing a polymer other than a polyacetal
in a high proportion which has been hitherto impossible
5 can be easily attained.

(4) Sticking of polymer to the inside of the
polymerization tank is minimal and the acetal copolymer
can be smoothly produced.

[Examples]

10 The present invention will be explained by the
following examples and comparative examples, but the
present invention is not to be limited by them.

Items of measurement and the methods for
measurement thereof in the examples and comparative
15 examples are as follows.

(1) Easiness in production technique:

Polymer slurry obtained in the polymerization
was filtered by a glass filter (G2, maximum pore
diameter 100-150 μ m) and easiness of polymerization was
20 evaluated by easiness in filtration and time required
for filtration. This evaluation is an indication of the
possibility of easy production of acetal copolymer with
respect to production technique.

The symbol "0" in the results of evaluation
25 means as follows:

0: Polymer slurry can be instantaneously
separated into particulate polymer and solvent
(colorless and transparent).

1 (2) Average particle size:

Average particle size of the particulate crosslinked polymer was measured by photography using an electron microscope.

5 (3) Average dispersion particle size:

Measurement was conducted using a customary particle size distribution measuring device (Coulter counter).

(4) Analysis of composition of acetal copolymer:

10 Proportions of the particulate crosslinked polymer and other polymer contained in the acetal copolymer were measured by the following method. That is, the resulting acetal copolymer was extracted for about 5 hours at the boiling point of an organic solvent (e.g.,
15 toluene) which can dissolve only the other polymer used as a molecular weight modifier or/and an organic solvent (e.g., hexafluoro isopropanol) which can dissolve only polyacetal. 5.0 g of acetal copolymer after being subjected to extraction was accurately weighed and added
20 to 100 ml of 1N hydrochloric acid and the polyacetal portion in the acetal copolymer was completely decomposed at 130°C for 2 hours. The residue after decomposition was washed and dried and the weight of the residue was measured and the proportions of the particu-
25 late crosslinked polymer and the other polymer in the acetal copolymer were obtained.

(5) Viscosity:

25 mg of acetal copolymer was dissolved in 5 ml of a mixed solvent (p-chlorophenol 50% by weight and

1 tetrachloroethane 50% by weight). Viscosity was measured using an Ostwald viscosity tube at 60°C. The viscosity is an indication of the molecular weight of the acetal copolymer.

5 (6) Measurement of properties:

① Tensile weld characteristics:

This was measured in accordance with ASTM D-638. The weld test was conducted using a test piece which forms a weld line at the center on a shape of a
10 test piece of double gate. Distance between chucks was 114 mm (standard) and pulling rate was 50 mm/min.

② Izod impact characteristics:

This was measured in accordance with ASTM D-256.

15 Example 1

(1) Preparation of particulate crosslinked polymer (A):

In a 10 l beaker provided with a stirrer and a condenser were charged 5.7 l of distilled water, 20 g of
20 sodium dioctylsulfosuccinate as an emulsifier, and 1.2 g of Rongalit as a reducing agent to carry out homogeneous dissolution.

Thereto was added a homogeneous solution of 1,270 g of n-butyl acrylate (hereinafter referred to as
25 "BA"), 320 g of styrene (hereinafter referred to as "St"), 20 g of diethylene glycol diacrylate (hereinafter referred to as "DEGA"), 1.6 g of diisopropylbenzene

1 hydroperoxide (hereinafter referred to as "PBP"), and
150 g of 2-hydroxyethyl methacrylate (hereinafter
referred to as "HEMA") as a graft-copolymerizable vinyl
monomer having a hydroxyl group and polymerization was
5 carried out at 80°C. Reaction was completed in about 40
minutes. Tg of the resulting polymer was -37°C.

Then, the polymer was heated to 95°C and was
left for 1 hour. The resulting polymer was introduced
into a 0.5% aqueous aluminum chloride solution to
10 agglomerate and the agglomerate was washed with warm
water five times and dried to obtain a white particulate
crosslinked polymer (A).

Average particle size of this particulate
crosslinked polymer was 0.21 μm .

15 (2) Preparation of acetal copolymer:

In 10 l of cyclohexane was suspended 1,060 g
of the particulate crosslinked polymer (A) obtained in
(1) at an average dispersion particle size of 150 μm .
Thereafter, to the cyclohexane were continuously fed
20 anhydrous formaldehyde at 2000 g/hr and tetrabutyl-
ammonium acetate as a polymerization catalyst at 0.30
g/hr for 1 hour, during which the polymerization
temperature was kept at 50°C.

The resulting polymer slurry contained
25 particulate polymer and when this polymer slurry was
filtered using a glass filter (G2), the slurry was able
to be separated easily and rapidly into particles and
solvent.

1 The particles were contacted with acetic
anhydride in the form of vapor to carry out terminal
stabilization, thereby to obtain an acetal copolymer of
the present invention.

5 The proportion of the particulate crosslinked
polymer (A) in the acetal copolymer was 33% by weight.
Viscosity of the acetal copolymer was 2.8 (dl/g).

A known stabilizer such as an antioxidant was
added to this acetal copolymer and the copolymer was
10 melt kneaded in a 30 mmφ twin-screw extruder having a
high shearing performance at a cylinder temperature of
200°C, a screw speed of 100 rpm, and a extrusion amount
of about 5 kg/hr to obtain pellets of the acetal
copolymer.

15 The pellets were sufficiently dried and
injection molded at a cylinder temperature of 200°C to
obtain a test piece. Evaluation was carried out of the
test piece.

Tensile weld characteristics are shown below.

20 Tensile weld characteristics (weld
portion/non-weld portion)

Strength (kg/cm ²)	Elongation (%)
288/292	59/67

This acetal copolymer had good weld character-
25 istics and had the mechanical properties excellent in
isotropy of the present invention. This copolymer also
had an excellent impact resistance of 63 kg cm/cm in
Izod impact value.

1 Comparative Example 1

A particulate crosslinked polymer (B) was prepared in the same manner as in Example 1 except that HEMA was not used. Furthermore, the procedure was
5 conducted in the same manner as in Example 1 except that acetic anhydride as a molecular weight modifier was fed at 3 g/hr in the preparation of the acetal copolymer.

A part of the resulting acetal copolymer was taken out and extracted with hexafluoro isopropanol.

10 Weight retention after extraction based on that before extraction was 36% by weight. This indicates that most of the polyacetal was extracted and removed and means that reaction bonding was not present between the polyacetal and the particulate crosslinked polymer (B).

15 Tensile weld characteristics of the resulting acetal copolymer are shown below.

Strength (kg/cm ²)	Elongation (%)
189/290	7/64

Thus, when the polyacetal and the particulate
20 crosslinked polymer were not reaction bonded because a particulate crosslinked polymer having no functional group was used, an acetal copolymer having mechanical properties excellent in isotropy was not obtained.

Izod impact value of this copolymer was low,
25 namely, 17 kg cm/cm.

1 Examples 2-5

 The procedure of Example 1 was repeated except
that the proportion of the particulate crosslinked
polymer in the acetal copolymer was changed and the same
5 evaluation was conducted. The results are shown in
Table 1. Good results were obtained for all proportions
of the particulate crosslinked polymer.

 Examples 6-8

 The procedure of Example 1 was repeated except
10 that the proportions of BA and St which constituted the
particulate crosslinked polymer were changed to change
the Tg of the particulate crosslinked polymer, and the
same evaluation was conducted. Good results were
obtained as shown in Table 1.

15 Examples 9-11

 The procedure of Example 1 was repeated except
that the addition amount of emulsifier was changed and
the average particle size of the particulate crosslinked
polymer was changed and the same evaluation was
20 conducted. The results are shown in Table 1. Acetal
copolymers having mechanical properties excellent in
isotropy in a wide average particle size range were
obtained.

 Examples 12-14

25 The procedure of Example 1 was repeated except
that the amount of HEMA was changed to change the number

1 of hydroxyl groups possessed by the particulate
crosslinked polymer and the same evaluation was
conducted. The results are shown in Table 1. Good
results were obtained in all of these Examples.

5 Example 15

(1) Preparation of particulate crosslinked
polymer (C):

A particulate crosslinked polymer (C) of two-
phase structure having a hard phase outside a soft phase
10 was prepared in the following manner.

A polymer constituting the soft phase was
prepared in the same manner as in Example 1 except that
1,270 g of BA, 320 g of St, 20 g of DEGA, and 13 g of
allyl methacrylate (hereinafter referred to as "ALMA")
15 were used as monomers for polymerization in place of
those used for preparation of the particulate
crosslinked polymer (A). Tg of the polymer was -38°C.

Next, for formation of the hard phase as the
outermost phase, thereto was added a homogeneous
20 solution of 680 g of methyl methacrylate (hereinafter
referred to as "MMA"), 4.0 g of BA, and 14 g of HEMA as
monomers and 0.6 g of PBP and 0.2 g of n-octylmercaptan
(hereinafter referred to as "OM") and polymerization was
carried out. Tg of the polymer obtained by single
25 polymerization of these monomers was 109°C. The
reaction at this stage terminated in about 15 minutes.

1 Furthermore, the same procedure as in Example
1 was carried out to obtain the white particulate
crosslinked polymer (C).

(2) Preparation of acetal copolymer:

5 An acetal copolymer was obtained in the same
manner as in Example 1 and evaluation thereof was
conducted in the same manner.

As shown in Table 2, this acetal copolymer had
mechanical properties excellent in isotropy. In this
10 way, an acetal copolymer having mechanical properties
excellent in isotropy can also be obtained using a
particulate crosslinked polymer having a two-phase
structure.

Examples 16-26

15 The procedure of Example 1 was repeated except
that the composition (graft-copolymerizable vinyl
monomer) and proportion of the particulate crosslinked
polymer were changed and the same evaluation was
conducted.

20 Results of the evaluation are shown in Table
2. In all of these Examples, the resulting acetal
copolymers had the mechanical properties excellent in
isotropy of the present invention.

Example 27

25 The procedure of Example 15 was repeated
except that 170 g of glycidyl methacrylate was used in

1 place of HEMA, thereby to obtain a particulate
crosslinked polymer (D).

Then, 5000 g of the particulate crosslinked
polymer (D), 15 kg of trioxane, 750 g of ethylene oxide,
5 0.50 g of boron trifluoride, and 50 g of methylal were
charged in a kneader having two sigma-type blades and
polymerization was carried out at 80°C for 45 minutes.
Subsequently, 1200 g of triethylamine and 5 kg of water
were added, followed by stirring at 150°C for 30 minutes
10 to stabilize the polymer. A stabilizer such as an
antioxidant was added to this polymer and the polymer
was pelletized by a 30 mm ϕ single-screw extruder and
evaluation was conducted as in Example 15.

The results are shown in Table 2. It can be
15 seen that the resulting acetal copolymer obtained in the
cationic polymerization system also had very good
results as in this Example.

Comparative Examples 2 and 3

Two kinds of particulate crosslinked polymers
20 having average particle sizes of 0.009 μ m and 11 μ m were
prepared in the same manner as in Example 1 except that
the amount of emulsifier was changed to change the
average particle size of the particulate crosslinked
polymer in the preparation of the particulate
25 crosslinked polymer (A).

Using these polymers, acetal copolymers were
prepared in the same manner as in Example 1. Results of

1 the evaluation of the resulting acetal copolymers are
shown in Table 3.

As can be seen from Table 3, an acetal
copolymer having high impact resistance characteristics
5 was not obtained when the average particle size was less
than 0.01 μm and weld characteristics of the acetal
copolymer decreased considerably when the average
particle size was more than 10 μm .

Comparative Examples 4 and 5

10 The procedure of Example 1 was repeated except
that the amount of HEMA was changed in the preparation
of the particulate crosslinked polymer (A) and the pro-
portion of the particulate crosslinked polymer in the
acetal copolymer was changed and evaluation was conduct-
15 ed as in Example 1. The results are shown in Table 3.

As shown in Table 3, tensile properties and
the Izod impact value of the resulting acetal copolymer
decreased greatly when the viscosity was less than 0.1.
Furthermore, when the viscosity was more than 10, the
20 resulting acetal copolymer was not able to be injection
molded and thus was not practical.

Example 28

2-Hydroxyethyl methacrylate modified ethylene-
propylene elastomer (hereinafter referred to as "modi-
25 fied EPR") was used as the other polymer. This modified
EPR had eight hydroxyl groups in the main chain and had

1 a number-average molecular weight of 6×10^4 and a
polypropylene content of 30% by weight. This modified
EPR was freeze-ground by a customary grinder at -160°C
to an average dispersion particle size of 150 μm .

5 In 10 l of dehydrated cyclohexane was
suspended 1,050 g of this modified EPR which had been
sufficiently dried under reduced pressure and dehydrated
in the form of particles having the average dispersion
particle size mentioned above. In a 12 liter polymeri-
10 zation tank filled with cyclohexane were continuously
fed the modified EPR at 250 g/hr, formaldehyde of 99.9%
purity at 1,000 g/hr, cyclohexane at 5 l/hr, and tetra-
butylammonium acetate as a polymerization catalyst at
0.15 g/hr for 4 hours, during which the polymerization
15 temperature was kept at 60°C .

The resulting polymer slurry contained the
polymer in particle form and when this polymer slurry
was filtered by a glass filter (G2), it was able to be
easily and rapidly separated into particles and polymer-
20 ization solvent. Substantially no polymer stuck to the
polymerization tank.

Furthermore, the particles were stabilized by
contacting them with acetic anhydride vapor to obtain
the acetal copolymer of the present invention.

25 The amount of the modified EPR introduced in
this acetal copolymer was 18.9% by weight and the
viscosity of the acetal copolymer was 4.1 (dl/g).

1 Then, a known stabilizer such as an anti-oxidant was added to the resulting acetal graft copolymer and, thereafter, the copolymer was melt kneaded by a 45 mm ϕ twin-screw extruder at a cylinder temperature of 210°C, a screw speed of 50 rpm, and an extrusion amount of 2 kg/hr to obtain pelletized acetal copolymer. The pellets were sufficiently dried and then injection molded at a cylinder temperature of 210°C to obtain a molded piece. This was subjected to measurement of tensile weld characteristics and Izod impact value.

Tensile weld characteristics (weld portion/non-weld portion)

Strength (kg/cm ²)	Elongation (%)
470/475	76/81

15 Izod impact value was 48 kg cm/cm which indicates a high impact resistance. The resulting acetal copolymer had mechanical properties excellent in isotropy.

Examples 29-32

20 The procedure of Example 28 was repeated except that the proportions of the modified EPR and HEMA were changed and evaluation was conducted as in Example 28. The results are shown in Table 4.

In all of these Examples, acetal copolymers were able to be produced easily with respect to production technique as required by the present invention.

- 1 Further, the resulting acetal copolymers had mechanical
properties excellent in isotropy.

Comparative Example 6

The procedure of Example 28 was repeated ex-
5 cept that 1,000 g of the modified EPR used was complete-
ly dissolved in 10 l of dehydrated toluene and this was
continuously fed into the cyclohexane at 250 g/hr.

The resulting polymer slurry was very highly
viscous and an acetal copolymer in the form of particles
10 was not seen in the polymerization solvent.

Filtration by glass filter (G2) required a
very long time for separating the acetal copolymer and
polymerization solvent from the polymer slurry and the
filtrate was somewhat cloudy. It was considered that
15 this is because acetal copolymer which had not yet
become particles entered into the filtrate. Thus, it
must be said that it was impossible to produce acetal
copolymer easily with respect to the actual production
technique. Furthermore, much polymer stuck to the
20 inside of the polymerization tank.

Comparative Example 7

The procedure of Example 1 was repeated except
that 2,000 g of the modified EPR used was completely
dissolved in 20 l of dehydrated toluene and the solution
25 was continuously fed into the cyclohexane at 500 g/h (of
modified EPR) in Comparative Example 1.

1 When the resulting polymer slurry was filtered
by glass filter (G2), no filtrate was obtained and thus
filtration was impossible.

 In this way, when the other polymer used is
5 completely dissolved in a solvent and is used, if the
proportion of the other polymer in the acetal copolymer
is high as in this comparative example, it is no longer
possible to produce acetal copolymer stably with respect
to the actual production technique.

10 Examples 33-38

 Example 28 was repeated except that various
other polymers were used in place of the modified EPR
and evaluation was conducted. The results are shown in
Table 4.

15 In all of these examples, it was possible to
produce acetal copolymers easily with respect to the
production technique as required by the present
invention. Furthermore, the resulting acetal copolymers
had mechanical characteristics excellent in isotropy.

20 Example 39

 As the other polymer, 5,000 g of glycidyl
methacrylate modified EPR ground to an average disper-
sion particle size of 45 μ m was charged into a kneader
having two sigma type blades and thereto were further
25 added 10 kg of trioxane, 500 g of ethylene oxide, 0.30 g
of boron trifluoride, and 30 g of methylal and

1 polymerization was carried out at 70°C for 60 minutes.
Then, 1,200 g of triethylamine and 5 kg of water were
added and stirring was conducted for 30 minutes at 70°C
to stabilize the polymer. To this polymer was added a
5 stabilizer such as an antioxidant and the polymer was
pelletized by a 50 mmφ single-screw extruder and,
thereafter, evaluation was conducted as in Example 28.

The results are shown in Table 4. As shown in
this example, the acetal copolymer obtained in the
10 cationic polymerization system also had mechanical
properties excellent in isotropy.

Examples 40-47

In the same manner as in Example 28, evalua-
tion was conducted using the other polymers having
15 functional group at a terminal (polymer ①). The
results are shown in Table 5.

In all of these examples, it was possible to
produce acetal copolymers easily with respect to the
production technique. Further, the resulting acetal
20 copolymer had mechanical properties excellent in
isotropy as required by the present invention.

Table 1

Example	Composition of particulate crosslinked polymer			Average dispersion particle size (μm)	Easiness in production technique		
	Vinyl monomer	Graft-copolymerizable vinyl monomer (proportion*)	Average particle size (μm)			Viscosity (dl/g)	Proportion ** (wt%)
2	BA, St	HEMA (8.5)	0.21	150	O	4.9	5
3	"	"	"	"	O	3.1	20
4	"	"	"	"	O	1.9	60
5	"	"	"	"	O	1.8	80
6	"	"	"	"	O	2.6	33
7	"	"	"	"	O	2.9	33
8	"	"	"	"	O	2.4	32
9	"	"	0.07	120	O	2.1	33
10	"	"	0.70	135	O	2.4	33
11	"	"	1.40	180	O	2.4	33
12	"	HEMA (0.9)	0.21	150	O	6.1	36
13	"	" (5.8)	"	"	O	3.4	34
14	"	" (21.3)	"	"	O	1.0	33

* Proportion of graft-copolymerizable vinyl monomer is % by weight based on total weight of particulate crosslinked polymer.

** Proportion is % by weight of particulate crosslinked polymer based on total weight of acetal copolymer.

- Cont'd-

Table 1 (Cont'd)

Characteristics of acetal copolymer		Notes
Tensile weld characteristics (weld portion/non-weld portion)		
strength (kg/cm ²)	Elongation (%)	
670 / 675	36 / 38	Izod impact value 13 kg cm/cm
492 / 501	54 / 58	" 38 "
198 / 200	70 / 80	" 72 "
181 / 190	85 / 84	" 75 "
297 / 310	56 / 57	Tg of particulate crosslinked polymer -21°C
331 / 343	50 / 54	" 0°C
317 / 348	47 / 47	" 12°C
291 / 290	58 / 62	
265 / 281	60 / 64	
258 / 281	59 / 71	
290 / 290	59 / 61	
284 / 291	63 / 64	
292 / 299	54 / 59	

Table 2

Ex-ample	Composition of particulate crosslinked polymer			Average disper-sion particle size (μm)	Easi-ness in produc-tion tech-nique
	Vinyl monomer	Graft-copolymerizable vinyl monomer (proportion*)	Average particle size (μm)		
15	BA, St/MMA, BA	HEMA (0.6)	4.5	400	0
16	BA, St	Acrylic acid (1.9)	0.9	600	0
17	BA, St	m-Aminostyrene (14.0)	0.06	40	0
18	2-Ethylhexyl acrylate	Acrylamide (21.4)	2.0	30	0
19	Butadiene, St	Methoxyvinyl (5.4)	4.9	470	0
20	Butadiene, St	Maleic anhydride (4.2)	7.2	800	0
21	Butadiene, MMA	2-Hydroxyethyl acrylate (5.4)	2.0	1700	0
22	St, MMA	Allyl alcohol (15.4)	0.5	0.09	0
23	Butadiene, St, acrylonitrile	Maleic acid (4.0)	0.7	60	0
24	Ethyl acrylate, St	Methoxyethyl methacrylate (24)	0.1	72	0
25	MMA	Methacrylamide (0.9)	0.6	1.4	0
26	BA, MMA	HEMA (18.1)	0.4	40	0
27	BA, st/MMA, BA	glycidyl methacrylate (6.9)	0.7	86	0

* Proportion of graft-copolymerizable vinyl monomer is % by weight based on total weight of particulate crosslinked polymer.

** Proportion is % by weight of particulate crosslinked polymer based on total weight of acetal copolymer.

- Cont'd-

Table 2 (Cont'd)

Characteristics of acetal copolymer			
Viscosity (dl/g)	Proportion ** (wt%)	Tensile weld characteristics (weld portion/non-weld portion)	
		strength (kg/cm ²)	Elongation (%)
7.9	33	310 / 320	50 / 57
2.1	16	518 / 520	45 / 49
1.4	20	490 / 500	50 / 56
0.4	81	167 / 171	89 / 89
1.7	16	589 / 600	36 / 41
1.9	18	559 / 571	43 / 48
1.6	20	689 / 700	28 / 29
0.2	61	801 / 803	25 / 26
1.4	43	429 / 481	46 / 49
0.4	72	196 / 200	72 / 80
4.8	18	830 / 841	15 / 17
7.0	5	691 / 701	20 / 21
2.1	27	280 / 290	60 / 61

Table 3

Comparative Example	Composition of particulate crosslinked polymer			Average dispersion particle size (μm)	Easiness in production technique		
	Vinyl monomer	Graft-copolymerizable vinyl monomer (proportion*)	Average particle size (μm)			Viscosity (dl/g)	Proportion ** (wt%)
2	BA, St	HEMA (8.5)	0.009	0.9	0	2.1	33
3	BA, St	HEMA (8.5)	. 11	1100	0	2.0	33
4	BA, St	HEMA (4.1)	0.6	70	0	0.009	32
5	BA, St	HEMA (0.04)	0.3	60	0	11	34

- Cont'd-

* Proportion of graft-copolymerizable vinyl monomer is % by weight based on total weight of particulate crosslinked polymer.

** Proportion is % by weight of particulate crosslinked polymer based on total weight of acetal copolymer.

Table 3 (Cont'd)

Characteristics of acetal copolymer		Notes
Tensile weld characteristics (weld portion/non-weld portion)		
strength (kg/cm ²)	Elongation (%)	
300 / 340	30 / 40	Izod impact value 8 kg cm/cm
151 / 301	11 / 60	
79 / 108	4 / 8	Izod impact value 0.9 kg cm/cm
-	-	Molding was impossible.

Table 4

Ex-ample	Composition of other polymer		Average disper-sion particle size (μm)	Easi-ness in produc-tion tech-nique
		Graft-copolymerizable vinyl monomer (proportion*)		
29	Modified EPR	HEMA (1.8)	80	0
30	"	" (5.2)	51	0
31	"	" (0.9)	240	0
32	"	" (6.9)	170	0
33	Ethylene-propylene-dicyclo-pentadiene copolymer	2-Hydroxyethyl acrylate (2.1)	50	0
34	High-density polyethylene	m-Aminostyrene (7.1)	600	0
35	Low-density polyethylene	Acrylic acid (2.5)	1700	0
36	Styrene-butadiene copolymer	Maleic anhydride (1.0)	700	0
37	Hydrogenated styrene-butadiene copolymer	Allyl alcohol (0.2)	80	0
38	Low-density polyethylene	Allyl alcohol (0.8)	90	0
39	Modified EPR	Glycidyl methacrylate (6.0)	45	0

* Proportion of graft-copolymerizable vinyl monomer is % by weight based on total weight of particulate crosslinked polymer.

** Proportion is % by weight of particulate crosslinked polymer based on total weight of acetal copolymer.

- Cont'd-

Table 4 (Cont'd)

Characteristics of acetal copolymer				
Viscosity (dl/g)	** Proportion (wt%)	Tensile weld characteristics (weld portion/non-weld portion) strength (kg/cm ²) Elongation (%)		
4.4	9.8	651/ 670	43 / 50	Izod impact value 23 kg cm/cm
2.0	70.1	251 / 260	114 / 120	
6.1	85.0	210 / 220	129 / 141	
4.9	60.1	268 / 279	98 / 99	
1.9	14.4	508 / 510	35 / 39	
1.0	10.9	619 / 630	38 / 39	
2.9	5.0	680 / 691	28 / 30	
4.6	26.7	389 / 400	57 / 61	Izod impact value 48 kg cm/cm
7.2	61.0	236 / 240	118 / 120	
3.0	12.0	610 / 612	43 / 43	
2.6	36.1	281 / 297	69 / 70	

Table 5

Ex-ample	Composition of other polymer		Average disper-sion particle size (µm)	Easi-ness in produc-tion tech-nique
		Functional group		
40	Polybutylene terephthalate, poly-tetra-methylene glycol copolymer	Hydroxyl group Carboxyl group	180	0
41	Nylon-6, polypropylene glycol copolymer	Amino group Carboxyl group	150	0
42	Polyurethane synthesized from 4,4'-diphenyl methane, diisocyanate, tetramethylene glycol, polytetramethylene glycol	Hydroxyl groups (two)	400	0
43	Polystyrene, polybutadiene copolymer	Hydroxyl group	80	0
44	Polyethylene terephthalate	Carboxyl groups (two)	40	0
45	Polybutylene terephthalate	Carboxyl groups (two)	210	0
46	Polycarbonate	Hydroxyl group	8	0
47	Polyphenylene ether	Hydroxyl group	10	0

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** Proportion is % by weight of particulate crosslinked polymer based on total weight of acetal copolymer.

- Cont'd-

Table 5 (Cont'd)

Characteristics of acetal copolymer				Notes
Viscosity (dl/g)	Proportion (wt%)	Tensile weld characteristics (weld portion/non-weld portion)		
		strength (kg/cm ²)	Elongation (%)	
2.9	25	391 / 400	40 / 51	Izod impact value 40 kg cm/cm
1.8	5.7	560 / 570	41 / 46	Izod impact value 18 kg cm/cm
1.6	30	401 / 420	68 / 71	Izod impact value 39 kg cm/cm
4.6	30	400 / 401	65 / 68	
3.6	10	580 / 582	47 / 51	
1.9	5	620 / 631	35 / 38	
3.1	33	704 / 720	29 / 31	
2.0	21	549 / 610	34 / 36	

1 Industrial Applicability

According to the present invention, it has become possible to produce acetal copolymers having mechanical properties excellent in isotropy industrially and easily with respect to production technique by reaction bonding a polyacetal and polymers other than polyacetals which have specific properties.



CLAIMS

1. An acetal copolymer composed of polyacetal units and particulate crosslinked polymer units which has a viscosity of 0.1-10 dl/g and comprises a polyacetal and a particulate crosslinked polymer other than a polyacetal which has a functional group selected from the group consisting of a hydroxyl group, a carboxyl group, an amino group, an amide group, an alkoxy group, an acid anhydride group, and an epoxy group and has an average particle size of 0.01-10 μm , said polyacetal and particulate crosslinked polymer being reaction bonded to each other through the functional group.
2. An acetal copolymer according to claim 1, wherein the particulate crosslinked polymer units comprise an acrylate ester, a methacrylate ester, a conjugated diene compound, an aromatic compound, or a nitrile compound.
3. An acetal copolymer according to claim 1, wherein the particulate crosslinked polymer units comprise a polymer having a glass transition temperature of lower than 25°C.
4. An acetal copolymer according to claim 1, wherein the particulate crosslinked polymer units have a multi-phase structure of two or more phases which comprise repeating soft and hard phases, the polymer constituting the soft phase having a glass transition temperature of lower than 25°C, and the polymer





constituting the hard phase having a glass transition temperature of 25°C or higher.

5. An acetal copolymer according to claim 4, wherein the particulate crosslinked polymer units have a two phase structure having the hard phase outside the soft phase.

6. An acetal copolymer according to claim 4, wherein the soft phase comprises an acrylate ester or a conjugated diene compound and the hard phase comprises a methacrylate ester, an aromatic compound or a nitrile compound.

7. An acetal copolymer according to claim 4, wherein the soft phase comprises n-butyl acrylate, 2-ethylhexyl acrylate, ethyl acrylate, isopropyl acrylate, butadiene, or styrene-butadiene and the hard phase comprises methyl methacrylate, ethyl methacrylate, propyl methacrylate, isobutyl methacrylate, styrene, or acrylonitrile.

8. An acetal copolymer according to claim 1, wherein the particulate crosslinked polymer has a particle size distribution of 0.01-20 μm .

9. An acetal copolymer according to claim 1, wherein the particulate crosslinked polymer has a hydroxyl group.

10. An acetal copolymer according to claim 1, which contains the particulate crosslinked copolymer in an amount of 1.0-90% by weight based on total weight of the acetal copolymer.





11. A process for producing an acetal copolymer composed of polyacetal units and polymer units other than polyacetals which comprises a polyacetal and a polymer other than a polyacetal which are reaction bonded to each other through a functional group mentioned below and which has a viscosity of 0.1-10 dl/g, said process comprising homopolymerizing formaldehyde or trioxane or copolymerizing formaldehyde or trioxane with a cyclic ether in the presence of a polymer other than a polyacetal which has a functional group selected from the group consisting of a hydroxyl group, a carboxyl group, an amino group, an amide group, an alkoxy group, an acid anhydride group, and an epoxy group and which has an average dispersion particle size of 0.01-2000 μm .

12. A process according to claim 11, wherein the polymer units other than polyacetals comprises a polymer having a glass transition temperature of lower than 25°C.

13. A process according to claim 11, wherein the polymer units other than polyacetals are particulate crosslinked polymer units.

14. A process according to claim 13, wherein the particulate crosslinked polymer units comprise an acrylate ester, a methacrylate ester, a conjugated diene compound, an aromatic compound, or a nitrile compound.

15. A process according to claim 13, wherein the particulate crosslinked polymer units have a multi-phase structure of two or more phases which comprise





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repeating soft and hard phases, the polymer constituting the soft phase having a glass transition temperature of lower than 25°C, and the polymer constituting the hard phase having a glass transition temperature of 25°C or higher.

16. A process according to claim 15, wherein the particulate crosslinked polymer units have a two phase structure having the hard phase outside the soft phase.

17. A process according to claim 15, wherein the soft phase comprises an acrylate ester or a conjugated diene compound and the hard phase comprises a methacrylate ester, an aromatic compound or a nitrile compound.

18. A process according to claim 15, wherein the soft phase comprises n-butyl acrylate, 2-ethylhexyl acrylate, ethyl acrylate, isopropyl acrylate, butadiene, or styrene-butadiene and the hard phase comprises methyl methacrylate, ethyl methacrylate, propyl methacrylate, isobutyl methacrylate, styrene, or acrylonitrile.

19. A process according to claim 13, wherein the particulate crosslinked polymer comprises a graft-copolymerizable vinyl monomer having a functional group selected from the group consisting of a hydroxyl group, a carboxyl group, an amino group, an amide group, an alkoxy group, an acid anhydride group, and an epoxy group.

20. A process according to claim 19, wherein the amount of the graft-copolymerizable vinyl monomer is





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0.05-30% by weight based on total weight of the particulate crosslinked polymer.

21. A process according to claim 12, wherein the polymer other than a polyacetal is an ethylene-propylene type, ethylene-propylene-diene type, styrene-diene type, or hydrogenated styrene-diene elastomer having a functional group in the main chain.

22. A process according to claim 11, wherein the polymer other than a polyacetal has a dispersion particle size distribution of 0.01-3000 μm .

23. A process according to claim 11, wherein the polymer other than a polyacetal has a hydroxyl group.

24. A process according to claim 11, wherein the amount of the polymer other than a polyacetal is 1.0-90% by weight based on the total weight of the acetal copolymer.

25. A process according to claim 11, wherein the homopolymerization of formaldehyde or trioxane or the copolymerization of formaldehyde or trioxane with a cyclic ether is carried out in an organic medium.



* C L M S *