Title: ACRYLIC COPOLYMER FOR PROCESSING AID OF VINYL CHLORIDE RESIN COMPOSITION, METHOD FOR PREPARING THE SAME AND VINYL CHLORIDE RESIN COMPOSITION CONTAINING THE SAME

Abstract: The present invention relates to an acrylic copolymer, a method of preparing the same and a vinyl chloride resin composition containing the same, more precisely an acrylic copolymer prepared by polymerization of vinyl chloride seed with a monomer mixture composed of (b) methyl methacrylate and (b) one or more monomers selected from the group consisting of alkyl acrylate and alkyl methacrylate, a method of preparing the same, and a vinyl chloride resin composition comprising the same. According to the present invention, the addition of the acrylic copolymer of the invention to the vinyl chloride resin composition results in the excellent compatibility, the improvement of gelation, fish-eye and flow mark inhibitory effect during calendaring and extruding without reducing secondary processability including transparency and elongation at high temperature and at the same time satisfies the required foaming properties including foaming magnitude and foaming cell stability for the foaming extrusion.
Description

ACRYLIC COPOLYMER FOR PROCESSING AID OF VINYL CHLORIDE RESIN COMPOSITION, METHOD FOR PREPARING THE SAME AND VINYL CHLORIDE RESIN COMPOSITION CONTAINING THE SAME

Technical Field

[1] The present invention relates to an acrylic copolymer for processing aid of a vinyl chloride resin composition, a method of preparing the same and a vinyl chloride resin composition containing the same, more precisely an acrylic copolymer that has excellent compatibility to improve gelation during melting process when it is added to a vinyl chloride resin composition, reduces fish-eye and flow mark generated during calendering or extruding processes without the decrease of secondary processability including transparency and elongation at high temperature, and at the same time has satisfactory foaming properties for foaming extrusion such as foaming magnitude and foaming cell stability, a method of preparing the same and a vinyl chloride resin composition containing the same.

Background Art

[2] Vinyl chloride resin is a polymer containing at least 50% of vinyl chloride, which is inexpensive, easy to regulate the hardness, applicable to most processing equipments, and facilitates the production of a composite having excellent physical and chemical characteristics, suggesting it can be applied to a variety of fields.

[3] However, this vinyl chloride resin has limitation in impact strength, processability, thermo-stability, and heat deformation temperature. To complement those weak points of the vinyl chloride resin, additives such as impact modifiers, processing aids, stabilizers and fillers have been developed and selectively used.

[4] As an attempt to make the weight of vinyl chloride resin light and to reduce the price of a molded part, foaming has been tried with stimulated interest. But, when vinyl chloride resin alone is used for foaming, elongation and melting strength are not satisfactory, resulting in poor outward appearance of a molded part, an uneven, big sized foaming cell and low foaming magnitude. To overcome those disadvantages, it has been generally tried to add an acrylic copolymer containing methyl methacrylate as a major component and a foaming agent to the vinyl chloride resin.

[5] US Patent No. 4,052,482 describes a method for processing vinyl chloride resin, in which fish-eye is prevented by the addition of a copolymer containing methyl methacrylate as a major component, transparency is improved and melting period is
shortened. However, the inhibitory effect on fish-eye in this method is not satisfactory.

US Patent No. 5,306,763 describes a method to reduce fish-eye by increasing the monomer content that has low glass transition temperature such as butyl acrylate. But, this method also has disadvantages of the decrease of melting viscosity resulted from the over-dose of butyl acrylate that makes process difficult and the generation of air-bubbles.

US Patent No. 5,541,256 describes a method to inhibit fish-eye during the production of polyvinyl chloride resin by adding a modifier prepared by using a cross-linking monomer. However, the introduction of the cross-linking monomer results in the decrease of secondary processability including elongation and tensile strength. And the inhibitory effect on fish-eye in this method is not satisfactory, either.

US Patent No. 6,140,417 describes a method tried to improve processability and expandability and to reduce fish-eye. According to this method, a large amount of butyl acrylate and a small amount of methyl methacrylate were used to produce a copolymer, and a monomer mixture composed of methyl methacrylate and acrylate was polymerized with the copolymer. A copolymer prepared by the polymerization of butyl acrylate and methyl methacrylate was added to the polymer product in order to inhibit fish-eye and to improve processability and expandability. However, there is still a chance of fish-eye problem owing to the irregularity of foaming cells.

Therefore, it is required to produce an acrylic copolymer for processing aid of a vinyl chloride resin composition with reducing fish-eye and flow marks during the vinyl chloride resin processing and at the same time with guaranteeing excellent expandability for the foaming extrusion.

Disclosure of Invention

Technical Problem

It is an object of the present invention, to overcome the above problems of conventional methods, to provide an acrylic copolymer that has excellent compatibility to reduce gelation during melting process when it is added to a vinyl chloride resin composition, and maintains its secondary processability including transparency and elongation at high temperature without being damaged during calendering or extruding, leading to the inhibition of fish-eye and flow marks, and has excellent foaming properties such as foaming magnitude and foaming cell stability in foaming extrusion, and a method of preparing the same.

It is another object of the present invention to provide a vinyl chloride resin composition containing the acrylic copolymer.

Technical Solution

The above objects of the present invention can be achieved by the following em-
bodiments of the present invention.

To achieve the above objects, the present invention provides an acrylic copolymer prepared by the polymerization of a vinyl chloride seed with a monomer mixture comprising (bl) methyl methacrylate and (b2) one or more monomers selected from the group consisting of alkyl acrylate and alkyl methacrylate.

The present invention also provides a method of preparing an acrylic copolymer resin, comprising the step of the emulsion polymerization of:

A) 1 - 10 weight parts of vinyl chloride seed and

B) 90 - 99 weight parts of a monomer mixture comprising (bl) 60 - 95 weight% of methyl methacrylate and (b2) 5 - 40 weight% of one or more monomers selected from the group consisting of alkyl acrylate and alkyl methacrylate.

The present invention further provides a vinyl chloride resin composition characteristically containing the acrylic copolymer by 1 - 20 weight parts for 100 weight parts of the vinyl chloride resin.

The present invention is described in detail hereinafter.

The present inventors have focused our study on an acrylic copolymer for processing aid of a vinyl chloride resin with reduced fish-eye and flow marks and excellent foaming properties for foaming extrusion. And the present inventors completed this invention by establishing the method in which a vinyl chloride seed is used to prepare an acrylic copolymer and the acrylic copolymer is added to the vinyl chloride resin, and further confirming that the product resin composition has excellent compatibility to reduce gelation during melting process when it is added to the vinyl chloride resin composition, and maintains its secondary processability including transparency and elongation at high temperature without being damaged during calendering or extruding, leading to the inhibition of fish-eye and flow marks, and has excellent foaming properties such as foaming magnitude and foaming cell stability in foaming extrusion.

The acrylic copolymer of the invention is characteristically prepared by the polymerization of a vinyl chloride seed with a monomer mixture comprising (bl) methyl methacrylate and (b2) one or more monomers selected from the group consisting of alkyl acrylate and alkyl methacrylate.

The acrylic copolymer is composed of (A) 1 - 10 weight parts of a vinyl chloride seed and (B) 90 - 99 weight parts of a monomer mixture comprising (bl) 60 - 95 weight% of methyl methacrylate and (b2) 5 - 40 weight% of one or more monomers selected from the group consisting of alkyl acrylate and alkyl methacrylate.

The vinyl chloride seed of (A) is prepared by the emulsion polymerization of 100 weight parts of a vinyl chloride monomer, 0.2 - 3 weight parts of an emulsifier, 0.001 - 2.0 weight parts of a polymerization initiator and 100 - 200 weight part of ion
exchange water.

The vinyl chloride seed of (A) is preferably 50 - 150 D in mean diameter, but not always limited thereto. When it has the mean diameter in the above range, the polymerization reactivity is excellent, resulting in excellent gelation characteristics during melting process due to the excellent stability of an acrylic copolymer, and foaming properties are also excellent owing to the increase of weight average molecular weight.

The preferable content of the vinyl chloride seed of (A) in 100 weight parts of the acrylic copolymer is 1 - 10 weight parts. The content within this range results in excellent compatibility, less fish-eye and flow marks and excellent foaming properties.

The monomer mixture of (B) for the polymerization with the vinyl chloride seed is composed of (b1) 60 - 95 weight% of methyl methacrylate and (b2) 5 - 40 weight% of one or more monomers selected from the group consisting of alkyl acrylate and alkyl methacrylate.

The preferable content of methyl methacrylate in 100 weight% of the monomer mixture is 60 - 95 weight%. The content within this range results in excellent compatibility with the vinyl chloride resin composition during calendering, resulting in excellent processability, and excellent dispersibility, resulting in the inhibition of the fish-eye.

The alkyl acrylate herein can be selected from the group consisting of linear alkyl acrylate having alkyl group of 1 - 18 carbon atoms such as methyl acrylate, ethyl acrylate, n-butyl acrylate, lauryl acrylate or stearyl acrylate, etc.; branched alkyl acrylate having 1 - 18 carbon atoms such as 2-ethylhexyl acrylate, etc.; and cyclic alkyl acrylate having 1 - 18 carbon atoms such as cyclohexyl acrylate, etc.

The alkyl methacrylate herein can be selected from the group consisting of linear alkyl methacrylate having alkyl group of 2 - 18 carbon atoms such as n-butyl methacrylate, lauryl methacrylate, stearyl methacrylate, tridecyl methacrylate, i-butyl methacrylate, t-butyl methacrylate and 2-ethylhexyl methacrylate, etc.; and cyclic alkyl methacrylate having 2 - 18 carbon atoms such as cyclohexyl methacrylate, etc.

The preferable content of one or more monomers selected from the group consisting of alkyl acrylate and alkyl methacrylate in 100 weight% of the monomer mixture is 5 - 40 weight%.

The preferable content of the monomer mixture of (B) in 100 weight parts of the acrylic copolymer is 90 - 99 weight parts. The content within this range results in the decrease of fish-eye and flow marks generated during the vinyl chloride resin processing process, and the improvement of foaming properties and stability in foaming extrusion.

The acrylic copolymer can be used as a processing aid of a vinyl chloride resin composition.
[32] The method of preparing the acrylic copolymer of the present invention is characterized by the polymerization of 1 - 10 weight parts of the vinyl chloride seed prepared by the emulsion polymerization and 90 - 99 weight parts of a monomer mixture containing 60 - 95 weight% of methacrylate and 5 - 40 weight% of one or more monomers selected from the group consisting of alkyl acrylate and alkyl methacrylate.

[33] The above polymerization is preferably the emulsion polymerization. It is well understood by those in the art that any conventional emulsifier, polymerization initiator and oxidoreductive catalyst can be used in the emulsion polymerization.

[34] The acrylic copolymer can be produced by the polymerization of 1 - 10 weight parts of the vinyl chloride seed and 90 - 99 weight parts of a monomer mixture with 0.5 - 5 weight parts of an emulsifier, 0.0005 - 0.005 weight part of a polymerization initiator, and 0.01 - 0.1 weight part of an oxidoreductive catalyst, based on 100 weight parts of the mixture of the vinyl chloride seed and the monomer mixture.

[35] Examples of the emulsifier include, but are not limited to one or more compounds selected from the group consisting of such anionic emulsifiers as aliphatic ester, alkyl benzene sulfonate, alkyl phosphate salt and dialkyl sulfosuccinate, etc.; and such nonionic emulsifiers as polyoxyethylene alkyl ether and alkylamine ester. It is preferred to include an emulsifier by 0.5 - 5 weight parts for 100 weight parts of the mixture of the vinyl chloride seed and the monomer mixture.

[36] The polymerization initiator can be selected from the group consisting of such water-soluble initiators as potassium persulfate, ammonium persulfate and sodium persulfate, etc.; such fat-soluble initiators including organic peroxides as t-butyl hydroperoxide, cumene hydroperoxide, benzoyl peroxide and lauryl peroxide; and redox initiators, etc. It is preferred to include a polymerization initiator by 0.0005 - 0.005 weight part for 100 weight parts of the mixture of the vinyl chloride seed and the monomer mixture.

[37] The oxidoreductive catalyst can be selected from the group consisting of sodium formaldehydesulfoxylate, disodium ethylenediaminetetraacetate, formaldehyde sodium sulfoxylate, ferrous sulfate, ethylenesodium diaminetetraacetate, and cupric sulfate. It is preferred to include an oxidoreductive catalyst by 0.01 - 0.1 weight part for 100 weight parts of the mixture of the vinyl chloride seed and the monomer mixture.

[38] The latex acrylic copolymer turns into acrylic copolymer in the powder form by the coagulation, dehydration, and drying processes.

[39] The acrylic copolymer powder can be applied to calendering, extrusion molding, blow molding, or injection molding, etc., and the resultant molded part has excellent secondary processability such as transparency and elongation at high temperature, which favors calendering. In case of applying to the foaming, it has advantages that the
foam with low foam density, even foaming cells and high stability is produced.

The vinyl chloride resin composition of the present invention characteristically comprises 1 - 20 weight parts of the acrylic copolymer for 100 weight parts of the vinyl chloride resin. When the acrylic copolymer content is in the above range, the original characteristics of vinyl chloride resin can be maintained and the secondary processability including transparency and elongation at high temperature is excellent, gelation is improved during the melting process, and the fish-eye and flow marks are reduced and at the same time foaming properties such as foaming magnitude and foaming cell stability are not damaged during the foaming extrusion.

The vinyl chloride resin composition can additionally include one or more additives selected from the group consisting of heat stabilizers, lubricants, processing aids, impact modifiers, plasticizers, UV stabilizers, flame retardants, coloring agents and fillers.

**Best Mode for Carrying Out the Invention**

Practical and presently preferred embodiments of the present invention are illustrative as shown in the following Examples.

However, it will be appreciated that those skilled in the art, on consideration of this disclosure, may make modifications and improvements within the spirit and scope of the present invention.

**[Examples]**

(A) Preparation of vinyl chloride seed

(A1) Vinyl chloride seed

To a 20 L high-pressure polymerization reactor equipped with a stirrer were added 4000 g of ion exchange water, 500 g of 5% sodium lauric acid solution, 3000 g of 5% sodiumdodecylbenzenesulfonate solution, and 500 g of vinyl chloride monomer. The temperature of the reactor was raised to 56°C, to which 500 g of 5% potassium persulfate solution was added, followed by the polymerization for 11 hours to give vinyl chloride seed of 100 Din mean diameter.

(AZ) Vinyl chloride seed

Polymerization was performed by the same manner as described above for the preparation of vinyl chloride seed in example (A1), except that vinyl chloride seed of 50 Din mean diameter was produced by adding 2000 g of ion exchange water, 500 g of 5% sodium lauric acid solution, 5000 g of 5% sodiumdodecylbenzenesulfonate solution, 5000 g of vinyl chloride monomer and 500 g of potassium persulfate solution.

(A3) Vinyl chloride seed

Polymerization was performed by the same manner as described above for the
preparation of vinyl chloride seed in example (Al), except that vinyl chloride seed of
150 D in mean diameter was produced by adding 5500 g of ion exchange water, 500 g
of 5% sodium lauric acid solution, 1500 g of 5% sodiumdodecylbenzenesulfonate
solution, 5000 g of vinyl chloride monomer and 500 g of potassium persulfate solution.

(A4) Vinyl chloride seed

Polymerization was performed by the same manner as described above for the
preparation of vinyl chloride seed in example (Al), except that vinyl chloride seed of
170 D in mean diameter was produced by adding 6000 g of ion exchange water, 500 g
of 5% sodium lauric acid solution, 1000 g of 5% sodiumdodecylbenzenesulfonate
solution, 5000 g of vinyl chloride monomer and 500 g of potassium persulfate solution.

(A5) Vinyl chloride seed

Polymerization was performed by the same manner as described above for the
preparation of vinyl chloride seed in example (Al), except that vinyl chloride seed of
40 D in mean diameter was produced by adding 1000 g of ion exchange water, 500 g of
5% sodium lauric acid solution, 6000 g of 5% sodiumdodecylbenzenesulfonate
solution, 5000 g of vinyl chloride monomer and 500 g of potassium persulfate solution.

Examples 1 12 and Comparative Examples 1 - 4: Preparation of acrylic copolymers

Example 1

To a 3 L four-necked flask reactor equipped with a stirrer, a thermometer, a
nitrogen inlet, and a circulating condenser were added 232 g of ion exchange water,
37.5 g of 8% fatty acid potassium salt solution, and a monomer mixture which was
prepared by mixing 75 g of the vinyl chloride seed latex of (Al) (solid content: 30 g,
mean diameter: 100D) with methyl methacrylate and butyl acrylate (85:15, 153 g of
methyl methacrylate was mixed with 27 g of butyl acrylate) to prepare an emulsion.
The temperature of the reactor was maintained at 40°C, to which 0.07 g of 10% t-butyl
hydroperoxide solution and 6.5 g of 4% activator solution were added in the presence
of nitrogen, followed by the first batch-type reaction. The activator solution was
composed of 0.017 g of disodium ethylenediaminetetraacetate (EDTA), 0.04 g of
formaldehyde sodium sulfoxylate (SFS), 0.001 g of ferrous sulfate and 1.392 g of ion
exchange water.

Upon completion of the first batch-type reaction, the reaction mixture was stirred
for one hour at the same temperature and then the temperature was regulated to 40°C,
to which 232 g of ion exchange water, 37.5 g of 8% fatty acid potassium salt solution,
and a monomer mixture of methyl methacrylate and butyl acrylate (85:15, 166 g of
methyl methacrylate was mixed with 29 g of butyl acrylate) were added to prepare an
emulsion. The temperature of the reactor was maintained at 40°C, to which 0.07 g of
10% t-butyl hydroperoxide solution and 6.5 g of the same activator solution as used for
the first batch-type reaction were added in the presence of nitrogen, followed by the second batch-type reaction.

Upon completion of the second reaction, stirring continued for 1.5 hour and the temperature of the reactor was maintained as 40°C, to which 232 g of ion exchange water, 37.5 g of 8% fatty acid potassium salt solution, and a monomer mixture of methyl methacrylate and butyl acrylate (85:15, 166 g of methyl methacrylate was mixed with 29 g of butyl acrylate) were added to prepare an emulsion. The temperature of the reactor was maintained as 40°C, to which 0.07 g of 10% t-butyl hydroperoxide solution and 6.5 g of the same activator solution as used for the first batch-type reaction were added in the presence of nitrogen, followed by the third batch-type reaction.

Upon completion of the third reaction, stirring continued for one hour to give a latex acrylic copolymer. The latex acrylic copolymer was turned into acrylic copolymer powder by coagulation, dehydration and drying.

Measurement of weight average molecular weight of acrylic copolymer

0.03 g of acrylic copolymer powder was dissolved in 10 Dover tetrahydrofuran (THF) for 24 hours, followed by measuring weight average molecular weight by gel permeation chromatography (GPC). The weight average molecular weight of the prepared acrylic copolymer was 3,500,000.

Example 2

An experiment was performed by the same manner as described in example 1, except that the vinyl chloride seed latex of 50 Din mean diameter (A2) was used.

Example 3

An experiment was performed by the same manner as described in example 1, except that the vinyl chloride seed latex of 150 Din mean diameter (A3) was used.

Example 4

An experiment was performed by the same manner as described in example 1, except that the monomer composed of methyl methacrylate and butyl acrylate at the ratio of 80:20 (144 g of methyl methacrylate and 36 g of butyl acrylate were used for the first reaction, and 156 g of methyl methacrylate and 39 g of butyl acrylate were used for the second and third reactions) was used.

Example 5

An experiment was performed by the same manner as described in example 4, except that the vinyl chloride seed latex of 50 Din mean diameter (A2) was used.

Example 6

An experiment was performed by the same manner as described in example 4, except that the vinyl chloride seed latex of 150 Din mean diameter (A3) was used.

Example 7
An experiment was performed by the same manner as described in example 4, except that the vinyl chloride seed latex of 170 Din mean diameter (A4) was used.

Example 8

An experiment was performed by the same manner as described in example 4, except that the vinyl chloride seed latex of 40 Din mean diameter (A5) was used.

Example 9

An experiment was performed by the same manner as described in example 4, except that 13.5 g (solid content: 5.4 g) of the vinyl chloride seed latex of 100 Din mean diameter (Al) was used along with the monomer mixture composed of 164 g of methyl methacrylate and 41 g of butyl acrylate for the first reaction.

Example 10

An experiment was performed by the same manner as described in example 4, except that 15 g (solid content: 6 g) of the vinyl chloride seed latex of 100 Din mean diameter (Al) was used along with the monomer mixture composed of 163 g of methyl methacrylate and 41 g of butyl acrylate for the first reaction.

Example 11

An experiment was performed by the same manner as described in example 4, except that 150 g (solid content: 60 g) of the vinyl chloride seed latex of 100 Din mean diameter (Al) was used along with the monomer mixture composed of 120 g of methyl methacrylate and 30 g of butyl acrylate for the first reaction.

Example 12

An experiment was performed by the same manner as described in example 4, except that 157.5 g (solid content: 63 g) of the vinyl chloride seed latex of 100 Din mean diameter (Al) was used along with the monomer mixture composed of 118 g of methyl methacrylate and 29 g of butyl acrylate for the first reaction.

Comparative Example 1

An experiment was performed by the same manner as described in example 1 except that the vinyl chloride seed latex of example 1 was not used and the monomer mixture composed of 179 g of methacrylate and 32 g of butyl acrylate was used for the first reaction.

Comparative Example 2

An experiment was performed by the same manner as described in example 4 except that the vinyl chloride seed latex of example 4 was not used and the monomer mixture composed of 168 g of methacrylate and 42 g of butyl acrylate was used for the first reaction.

Comparative Example 3

233 g (solid content: 95 g) of the acrylic copolymer latex prepared in comparative example 2 and 12.5 g (solid content: 5 g) of the vinyl chloride seed latex of 100 Din
mean diameter (Al) were mixed, followed by coagulation with calcium chloride, dehydration, and drying to give acrylic copolymer powder (the content of the acrylic copolymer latex was regulated according to the solid content).

Comparative Example 4

233 g (solid content: 95 g) of the acrylic copolymer latex prepared in comparative example 2 was coagulated with calcium chloride, dehydrated and dried to give powder. 12.5 g (solid content: 5 g) of the vinyl chloride seed latex of 100 Din mean diameter (Al) was coagulated with calcium chloride, dehydrated and dried to give powder. The acrylic copolymer powder and the vinyl chloride seed (Al) powder were mixed.

Experimental Examples 1 - 16: Preparation of vinyl chloride resin compositions using the acrylic copolymer

Experimental Example 1

(1) Preparation of a vinyl chloride resin composition

To 100 g of the vinyl chloride resin (LS080, LG Chem., Ltd., Korea) were added 6.4 g of KD-105 (the heat stabilizer and foam stabilizer prepared by mixing a heat stabilizer evenly with a lubricant, Dansuk Industrial Co., Ltd., Korea) and 14 g of a filler (CaCO₃). To the mixture were added 5 g of the acrylic copolymer prepared in example 1 and 0.8 g of azodicarbonamide, followed by mixing in Henschel mixer with increasing the temperature to 115°C to give a vinyl chloride resin composition containing the acrylic copolymer.

(2) Measurement of melting time of the vinyl chloride resin composition

64g of the vinyl chloride resin composition prepared in experimental example (1) was put in the Braabender spinning at 40 rpm at 180°C and the time taken from the minimum loading to the maximum loading was measured. The melting time measured thereby is shown in Table 1.

(3) Measurement of foaming properties of the vinyl chloride resin composition

The vinyl chloride resin composition prepared in experimental example (1) was put in a 30 D single spindle extruder equipped with a rectangular slit die to extrude the composition as a rectangular rod (5 Din thickness x 30 Din width) at the screw speed of 30 rpm at the cylinder temperature of 180°C. Then the rod was cut by 5 Din length. The foaming density of the resultant foam was measured by using a density meter and the results are shown in Table 1. As foaming density increased, foaming magnitude was reduced and thus foaming properties became poor.

The section of the foam obtained above was observed under the optical microscope. And 5 points were given to the even foaming cells, 3 points were given to the medium regular foaming cells (even and uneven foaming cells were mixed) and 1 point was given to the irregular foaming cells. The results are shown in Table 1.

(4) Measurement of fish-eye of the vinyl chloride resin composition
A filler was not added to prepare a vinyl chloride resin composition. The vinyl chloride resin composition was extruded as 0.2 D thick film from a 20 D single-spindle extruder equipped with a T-die at the screw speed of 30 rpm and at the cylinder temperature of 180°C. The fish-eyes in a certain region of the film surface were counted. 5 points were given when fish-eye was hardly observed. 3 points were given when fish-eyes were generated a few. 1 point was given when fish-eyes were generated a lot. The results are shown in Table 1.

**Experimental Example 2**

A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in example 2 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated and the results are shown in Table 1.

**Experimental Example 3**

A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in example 3 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated and the results are shown in Table 1.

**Experimental Example 4**

A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in example 4 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated and the results are shown in Table 1.

**Experimental Example 5**

A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in example 5 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated and the results are shown in Table 1.

**Experimental Example 6**

A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in example 6 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated and the results are shown in Table 1.

**Experimental Example 7**

A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in example 7 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated and the results are shown in Table 1.

**Experimental Example 8**
A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in example 8 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated and the results are shown in Table 1.

Experimental Example 9

A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in example 9 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated and the results are shown in Table 1.

Experimental Example 10

A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in example 10 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated and the results are shown in Table 1.

Experimental Example 11

A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in example 11 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated and the results are shown in Table 1.

Experimental Example 12

A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in example 12 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated and the results are shown in Table 1.

Experimental Example 13

A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in comparative example 1 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated and the results are shown in Table 1.

Experimental Example 14

A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in comparative example 2 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated and the results are shown in Table 1.

Experimental Example 15

A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in comparative example 3 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated
and the results are shown in Table 1.

**Experimental Example 16**

A vinyl chloride resin composition was prepared using the acrylic copolymer prepared in comparative example 4 by the same manner as described in experimental example 1. Melting time, foaming properties and fish-eye generation were investigated and the results are shown in Table 1.

**Table 1**

<table>
<thead>
<tr>
<th>Vinyl chloride seed</th>
<th>Monomer mixture MMA:BA (weight ratio)</th>
<th>Acrylic copolymer</th>
<th>Melting time (s)</th>
<th>Fish-eye</th>
<th>Foaming property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean diameter (μm)</td>
<td>Weight average molecular weight (×10^4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Example 1</td>
<td>100</td>
<td>5</td>
<td>85:15</td>
<td>350</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>5</td>
<td>85:15</td>
<td>370</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>5</td>
<td>85:15</td>
<td>340</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>5</td>
<td>80:20</td>
<td>370</td>
<td>4</td>
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<tr>
<td>5</td>
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<td>5</td>
<td>80:20</td>
<td>350</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>150</td>
<td>5</td>
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<td>100</td>
<td>10.5</td>
<td>80:20</td>
<td>330</td>
<td>12</td>
</tr>
</tbody>
</table>

| Comparative example | | | | | |
|---------------------|-------------------|-----------------|----------|----------|
| Example 1 | - | - | 85:15 | 340 | 1 | 95 | 3.5 | 0.85 | 4.0 |
| 3 | 100 | 5 | 80:20 | 350 | 14 | 92 | 3.5 | 0.85 | 4.0 |
| 4 | 100 | 5 | 80:20 | 350 | 15 | 108 | 4.0 | 0.87 | 4.0 |
| 16 | 112 | 3.5 | 0.89 | 3.5 |

As shown in Table 1, the vinyl chloride resin compositions of experimental examples 1 - 12 containing the acrylic copolymers prepared in examples 1 - 12 which were prepared by the polymerization of the vinyl chloride seed with the monomer mixture were confirmed to have excellent compatibility with vinyl chloride resins, excellent foaming properties and improved fish-eye inhibitory effect, compared with the vinyl chloride resin compositions of experimental examples 13 - 14 containing the acrylic copolymers of comparative examples 1 - 2 which did not contain the vinyl chloride seed.

Particularly, when the acrylic copolymers of examples 1 - 6 prepared by using the vinyl chloride seeds of 50 - 150 Din mean diameter were applied to the vinyl chloride resin compositions (experimental examples 1 - 6), the resultant compositions had excellent compatibility with vinyl chloride resin, improved gelation during melting process, inhibitory effect on fish-eye generation, low foam density, and even foaming cells, owing to the polymerization of the vinyl chloride seed. In the meantime, when the acrylic copolymer of example 7 prepared by using the vinyl chloride seed of 170 D
in mean diameter was used, the final acrylic copolymer had too big particle size, resulting in the decrease of weight average molecular weight with the decrease of latex stability. Thus, when the acrylic copolymer of example 7 was used for the vinyl chloride resin composition (experimental example 7), foaming cell uniformity was reduced. When the acrylic copolymer of example 8 prepared by using the vinyl chloride seed of 40 Dn mean diameter was used, the polymerization reactivity was reduced with reducing the polymerization conversion rate, and particularly when the acrylic copolymer of example 8 was added to the vinyl chloride resin composition (experimental example 8), fish-eye inhibitory effect was reduced. So, the preferable mean diameter of the vinyl chloride seed was determined to be 50 - 150 D.

When the acrylic copolymers of examples 1 - 8 and 10 - 11 prepared with 1 - 10 weight parts of the vinyl chloride seed were applied to the vinyl chloride resin compositions (experimental examples 1 - 8 and 10 - 11), fish-eye inhibitory effect and foaming properties were excellent. In the meantime, when the acrylic copolymer of example 9 prepared with 0.9 weight part of the vinyl chloride seed was added to the vinyl chloride resin composition (experimental example 9), compatibility with the vinyl chloride resin was not effective, gelation during melting process was not improved, and fish-eye inhibitory effect was not guaranteed, although foaming properties were great. When the acrylic copolymer of example 12 prepared with 10.5 weight parts of the vinyl chloride seed was applied to the vinyl chloride resin composition (experimental example 12), compatibility with the vinyl chloride resin was excellent, gelation during melting process was improved, fish-eye inhibitory effect was great, but melting time was extended. Therefore, the preferable content of the vinyl chloride seed for the acrylic copolymer polymerization was determined to be 1 - 10 weight parts.

In the case of the copolymer of comparative example 3 which was prepared by mixing the vinyl chloride seed with the acrylic copolymer latex and then prepared as powder and the copolymer of comparative example 4 prepared by mixing the vinyl chloride seed powder with the acrylic copolymer powder, when they were applied to the vinyl chloride compositions (experimental examples 15 - 16), melting time was extended, compatibility was not good, fish-eye inhibitory effect was reduced, and foaming properties were poor in both cases, so the foam product with excellent properties was not expected.

**Industrial Applicability**

As explained hereinbefore, the addition of the acrylic copolymer prepared by the polymerization of the vinyl chloride seed with the monomer mixture to the vinyl chloride resin composition results in excellent compatibility with the vinyl chloride
resin, and at the same time improves gelation during melting process, reduces fish-eye and flow mark generated during calendering or extruding without decrease of secondary processability including transparency and elongation at high temperature, and satisfies the required foaming properties including foaming magnitude and foaming cell stability for the foaming extrusion.
Claims

[1] An acrylic copolymer prepared by the polymerization of a vinyl chloride seed with a monomer mixture comprising (b1) methyl methacrylate and (b2) one or more monomers selected from the group consisting of alkyl acrylate and alkyl methacrylate.

[2] The acrylic copolymer according to claim 1, comprising:
A) 1 - 10 weight parts of vinyl chloride seed and
B) 90 - 99 weight parts of a monomer mixture comprising:
(b1) 60 - 95 weight% of methyl methacrylate and
(b2) 5 - 40 weight% of one or more monomers selected from the group consisting of alkyl acrylate and alkyl methacrylate.

[3] The acrylic copolymer according to claim 1 or claim 2, wherein the vinyl chloride seed is prepared by the emulsion polymerization of 100 weight parts of a vinyl chloride monomer, 0.2 - 3 weight parts of an emulsifier, 0.001 - 2.0 weight parts of a polymerization initiator, and 100 - 200 weight part of ion exchange water.

[4] The acrylic copolymer according to claim 1 or claim 2, wherein the mean diameter of the vinyl chloride seed is 50 - 150 μm.

[5] The acrylic copolymer according to claim 1 or claim 2, wherein the alkyl acrylate has the carbon number of alkyl group of 1 - 18 and is one or more compounds selected from the group consisting of methyl acrylate, ethyl acrylate, n-butyl acrylate, lauryl acrylate, stearyl acrylate, 2-ethylhexyl acrylate and cyclohexyl acrylate.

[6] The acrylic copolymer according to claim 1 or claim 2, wherein the alkyl methacrylate has the carbon number of alkyl group of 2 - 18 and is one or more compounds selected from the group consisting of n-butyl methacrylate, lauryl methacrylate, stearyl methacrylate, tridecyl methacrylate, i-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate and cyclohexyl methacrylate.

[7] The acrylic copolymer according to claim 1, wherein the acrylic copolymer is used as a processing aid of a vinyl chloride resin composition.

[8] A method of preparing an acrylic copolymer resin comprising the step of the emulsion polymerization of:
A) 1 - 10 weight parts of vinyl chloride seed and
B) 90 - 99 weight parts of a monomer mixture comprising:
(b1) 60 - 95 weight% of methyl methacrylate and
(b2) 5 - 40 weight% of one or more monomers selected from the group consisting of alkyl acrylate and alkyl methacrylate.
[9] A vinyl chloride resin composition comprising the acrylic copolymer of claim 1 by 1 - 20 weight parts for 100 weight parts of a vinyl chloride resin.

[10] The vinyl chloride resin composition according to claim 9, wherein the vinyl chloride resin composition additionally includes one or more additives selected from the group consisting of heat stabilizers, lubricants, processing aids, impact modifiers, plasticizers, UV stabilizers, flame retardants, coloring agents and fillers.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

C08F 259/04(2006.01)Ji

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8 C08F

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☐ Further documents are listed in the continuation of Box C ☒ See patent family annex

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Date of the actual completion of the international search 24 DECEMBER 2007 (24.12.2007)
Date of mailing of the international search report 24 DECEMBER 2007 (24.12.2007)

Name and mailing address of the ISA/KR

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Facsimile No 82-42-472-7140

Authorized officer

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## International Search Report

### Information on patent family members

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