

Description

This invention relates in general to extrusion-grade vinylidene chloride copolymer compositions and, additionally, to films prepared therefrom.

While many different materials, e.g., waxed papers, plastic coated papers, aluminum foil, and polyethylene film are used as protective wrapping, vinylidene chloride copolymer films are most widely used because of their low water and gas vapor transmission properties and resistance to mechanical and chemical deterioration as well as their adaptability to microwave cooking. In many instances, however, the vinylidene chloride copolymer film does not have sufficient cling and cohesion properties to adhere to itself when a small amount of pressure is applied as in household applications and, therefore, often does not adequately seal-in flavor, moisture, and other desirable properties of fresh or prepared food items.

Accordingly, various additives are frequently incorporated into the vinylidene chloride copolymer compositions from which film is made in order to increase the cling properties of the resulting film. In the case of extrusion grade vinylidene chloride copolymer compositions, for example, such additives are frequently in the form of liquids, such as citric acid esters, which typically perform the dual function of a cling enhancer as well as a plasticizer or extrusion aid.

Although the aforementioned additives have been useful in imparting cling properties to vinylidene chloride copolymer films containing them, such additives have introduced new problems. For example, the liquid cling additives have limited solubility in the vinylidene chloride copolymer resin and will sometimes exude to the surfaces of the film and excessively plate-out on, or transfer to, contacting members of film-making or film-handling machinery, thereby causing irregularities in the operation of such machinery or in the quality of the product.

Known additives are also incapable of providing high-cling properties while maintaining a balance of other physical properties. Although high-cling properties, which are required in films used for industrial and consumer applications, can be achieved with the known additives by increasing the amount thereof, such increased cling is attended by a loss of good processability and handleability. Either the films cling too much to themselves and present severe problems in handling because they cannot readily be pulled apart, (i.e., "a blocking" effect), or they are readily handleable but exhibit poor cling properties. In addition to the handleability problems effected by increasing the amount of such additives, other deleterious properties, such as increased oxygen permeability and cost, as well as decreased modulus of the film, tend to occur.

Accordingly, it is desirable to provide an extrusion grade vinylidene chloride copolymer composition capable of producing a film having inherent cling properties sufficient to enable it to form a seal upon the application of a small amount of pressure, yet which seal can be readily pulled apart. Furthermore, it would be desirable to provide such a high-cling/low-blocking film wherein the aforementioned problems of high oxygen permeability and cost, and decreased modulus are not as pronounced as in the past. It is also advantageous to provide such a composition having low vinylidene chloride and vinyl chloride residuals and low exudation of such additives over a period of time, which is easy to extrude and relatively inexpensive, has high-cling and is relatively stiff. This invention provides such a novel composition.

The present invention resides in a high cling film comprising an extrudable resin composition comprising:

- (a) a vinylidene chloride copolymer in which a major proportion of the copolymer is a vinylidene chloride monomer with a minor proportion of at least one other polymeric comonomer, and
- (b) less than 10 percent by weight of total resin composition of a polymer blend consisting of a grease copolymer having a peak molecular weight of from 500 to 7500 as determined by gel permeation chromatography and a non-polymeric ester plasticizer.

Vinylidene chloride copolymers (Saran®) which can be used in the practice of this invention are any copolymers which are obtained by copolymerizing a major proportion of vinylidene chloride monomer with at least one other comonomer and which are capable of forming a film product under extrusion conditions. Typically, such extrusion grade vinylidene chloride copolymers are crystalline in the normal state and contain from 70 to 95 weight percent of vinylidene chloride, with the remainder comprising one or more ethylenically unsaturated comonomers, such as vinyl chloride, vinyl acetate, vinyl propionate, acrylonitrile, alkyl and aralkyl (butyl) acrylates and methacrylates having alkyl and aralkyl groups of up to about 8 carbon atoms, acrylic acid, acrylamide, vinyl alkyl ethers, vinyl alkyl ketones, acrolein, allyl esters and ethers, butadiene, chloroprene and others. Representative ternary compositions which may be used include the polymers of vinylidene chloride with, for example, acrolein and vinyl chloride; acrylic acid and acrylonitrile; alkyl acrylates and alkyl methacrylates; acrylonitrile and butadiene; acrylonitrile and itaconic acid; acrylonitrile and vinyl acetate, vinyl propionate, or vinyl chloride; alkyl esters or ethers and vinyl chloride; butadiene and vinyl acetate, vinyl propionate, or vinyl chloride; and vinyl ethers and vinyl chloride. Quaternary and higher polymers of similar monomeric compositions, as well as blends of vinylidene chloride copolymers, may also be used advantageously.

The vinylidene chloride copolymers can be made by any manner suitable for preparing extrusion grade resins of such copolymers such as by polymerization in mass or in an aqueous medium through the techniques of suspension or emulsion polymerization.

65 ® Registered Trade Mark.



Grease copolymers suitable for use as a cling enhancing additive with the vinylidene chloride copolymers of this invention are generally characterized as greases or oils. Typically, such grease copolymers have peak molecular weights, as determined by gel permeation chromatography, in the range from 500 to 7500, preferably from 1000 to 4000. Gel permeation chromatographic methods for determining molecular weights of polymers are described by J. C. Moore in the *J. Polymer Sci. A*, 2, 835 (1964). See also L. H. Tung, *J. Appl. Polymer Sci.*, 10, 345 (1966) and W. N. Smith, *J. Appl. Polymer Sci.*, 11, 639 (1967). Since such copolymers have melt flow rates above those which can be accurately measured by ASTM D-1238-70(E) at 190°C and 2.16 kilograms, it is necessary to alter some of the conditions of this test method in order to obtain more meaningful values. Using the apparatus and procedures of ASTM D-1238-70(E) except that the diameter of the plastometer orifice is reduced to 0.50 ± 0.005 mm and the test temperature is 80°C, the grease copolymers utilized in this invention exhibit melt flow rates in the range from 5 to 50, preferably from 10 to 25, decigrams/minute (dg/min).

The low molecular weight or grease copolymers can be prepared by polymerizing the corresponding monomers at high temperatures and pressures in the presence of a free radical catalyst. While forming the grease copolymer is not part of this invention, a suitable means of preparation is described in U.S. Patent 2,395,381 except that higher temperatures and increased catalyst concentration are used. In a preferred method up to about 20 weight percent based on the total comonomer weight of a telomer such as ethylene or propylene is added to the polymerization zone to inhibit the formation of high molecular weight copolymers.

Preferred grease copolymers of ethylene and vinyl acetate ("EVA") which can be used generally comprise from 10 to 55 weight percent, preferably from 35 to 50 weight percent vinyl acetate, including the partially hydrolyzed derivatives thereof. Minor amounts of other copolymerizable monomers can also be included in the copolymer, so long as they do not deleteriously affect the properties thereof.

The amount of a polymeric blend of the grease copolymer with a conventional plasticizer to be added to the extrusion grade vinylidene chloride copolymer will depend upon the degree of cling properties and stiffness desired in the film product. The proportion of the grease copolymer/plasticizer blend is from an effective cling-enhancing amount to less than 10, by weight of the total resin composition of the polymer blend, preferably from 0.1 to 7, and most preferably from 3.0 to 7.0 weight percent of the extrusion grade composition. This use of less than 10 weight percent of the copolymer blend achieves the desired results without adversely affecting the essential visual characteristics, i.e., the clarity, of the film product. The actual amount required to achieve the desired cling properties will vary with molecular weight of the grease copolymer and the proportion of ester comonomer in the copolymer.

The most desirable embodiments of the present invention comprehend a blend of a conventional plasticizer with the grease copolymer since a 100 percent application of the grease copolymer can result in handling or processing difficulties because of the tackiness of the grease copolymer. In a blend of the grease copolymer and plasticizer, as the amount of grease copolymer decreases with respect to the amount of the plasticizer, the modulus or stiffness of the film has been found to decrease significantly. This relationship is demonstrated in the Examples in the Table I.

The examples in Table I were conducted with an ethylene/vinyl acetate grease copolymer/plasticizer blend comprising between 3 to 6 percent of the entire composition. The composition also included from 1.0 to 1.5 percent by weight of a stabilizer of an epoxidized soy bean oil (9-62). The plasticizers blended with the EVA grease copolymer were selected from Citroflex® A-4, a citric acid (non-polymeric) ester di-octyl adipate (DOA), and di-iso butyl adipate (DIBA). Actual numbers in Table I show a decrease in modulus as the ratio of conventional plasticizer is increased in proportion to the EVA grease copolymer. Table I illustrates the effect of increasing the percentage of EVA grease copolymer to the plasticizer. As the amount of the plasticizer is decreased and the EVA grease copolymer increased, the modulus increases.

A ratio of from 20 percent plasticizer to 80 percent EVA grease copolymer and from 80 percent plasticizer to 20 percent grease copolymer essentially alleviates any handling and processing difficulties as compared to using 100 percent EVA grease copolymer yet still provides a film having an exceptionally high modulus of greater than about 5300 kg/cm². Thus, an economical vinylidene chloride copolymer film with the desired stiffness and processability was achieved with the plasticizing component in the composition being an EVA grease copolymer/plasticizer blend of the type hereinbefore described. It will be recognized, however, that as the percentage of the plasticizer increases with respect to the EVA grease copolymer, stiffness is sacrificed.

Where needed or desired, conventional additives may be included with the extrusion grade composition, such as heat stabilizers and the like. Antioxidants, such as those used with conventional cling additives, have not been found to be necessary for the grease copolymers used in the present invention. If desired, however, a minor amount of such materials may be used.

Mixing of the extrusion grade vinylidene chloride copolymer with a grease copolymer/plasticizer blend, plus other additives, if any, can be carried out in conventional resin blending processes and equipment, such as homogenizing blenders or possibly mixing extruders. It is advantageous that all components be as thoroughly mixed as possible so as to improve the cling efficiency contributed by the low molecular weight grease copolymer. Due to the viscous nature of the grease copolymer additive, it is particularly advantageous for thorough mixing that the low molecular weight copolymer be slightly heated before being mixed with the vinylidene chloride copolymer. With a grease copolymer/conventional

plasticizer blend, heating may be optional. Although not the only method, a most beneficial and convenient method of obtaining thorough mixing comprises adding the grease copolymer/conventional plasticizer blend to the polymerization reactor with the monomers used to prepare the vinylidene chloride copolymer. In larger reactors used for polymerization in an aqueous medium, however, care should be taken to avoid adding the grease copolymer/plasticizer blend after the dispersion of monomers has been formed, since such could create a layer of copolymer on the surface of the aqueous medium which would later interfere with the addition of a polymerization terminator, as such is frequently practiced in the art.

Compositions of the vinylidene chloride copolymer and low molecular weight grease copolymer/plasticizer blends, prepared by any of the aforementioned variations, can be formed into a thin film by any of the conventional methods known for making films from vinylidene chloride copolymers, such as by the cast film process or the trapped bubble/blown film process. Films made in accordance with this invention range in thickness from 0.2 mil (0.0051 mm) to 3.0 mil (0.076 mm), preferably from 0.4 mil (0.0102 mm) to 1 mil (0.0254 mm).

The examples in the following Tables illustrate the invention but are not to be taken as limiting its scope. In the examples, parts and percentages are by weight unless otherwise indicated.

Films were tested for cling by a method consisting of preparing a first portion and a second portion of the film to be tested, both portions having dimensions of 12.7 cm by 20.3 cm. The first portion is then secured lengthwise, i.e., by taping the ends, to the upper surface of a metal plate which is inclined 30° from horizontal and securely mounted on a top-loading balance. The second portion of film is then superimposed upon the first in a face-to-face relationship and the uppermost edge of the second portion is secured by taping leaving the lowermost edge of the second portion free. It is essential that the portions be superimposed without wrinkles, creases, or bubbles. The lowermost, free edge of the second portion is then clamped and attached to a wire hanger, which is in turn attached to the bottom of a movable cart. The cart travels by a system of pulleys and motor upon a raised, inclined track in such fashion that the free end of the second portion of the film will be pulled upward away from the first portion in a continuous vertical direction, thereby peeling or separating the two portions of film so as to propagate the peeled front at a constant rate of 12.7 cm per minute. The average force (in grams) required to separate the two portions is then read from the balance.

Block, which is essentially long-term cling, is measured by carefully removing intact two superimposed film portions from a roll of film which had been aged more than one week, and then determining the force required to separate the film portions in a manner similar to that used for measuring cling.

Runs were made comparing the physical characteristics of films prepared by blending from 3 to 6 percent by weight of an ethylene vinyl-acetate grease copolymer/plasticizer blend to a vinylidene chloride copolymer, with varying amounts of the EVA grease copolymer with respect to the plasticizer. The ratio of grease copolymer to plasticizer ranged from as high as 80 percent of the blend to as low as 20 percent. All films were aged for a period of 15 days prior to testing for 2% Secant Modulus and were aged for 30 days prior to testing for cling and block by the aforementioned procedure.

All the films according to the invention had a cling value of at least 5 grams after aging for 30 days and a stiffness in excess of 5300 kg/cm² as defined by a 2% Secant Modulus test.

TABLE I

(12)

Run No.	EVA-Grease copolymer (%)	Plasticizer (%)	Cling (grams)	Block (grams)	2% Secant modulus kg/cm ²	2% Secant modulus MPa
5						
1	1.0	2.0	5.5	8.0	7698	755
2	2.0	1.0	5.0	7.0	8626	846
10						
3	2.0	2.0	7.0	9.5	6608	648
4	2.0	2.0	6.5	8.0	7241	710
5	2.0	3.0	8.0	9.5	6165	605
15						
6	2.5	2.5	8.5	9.0	6404	628
7	3.0	2.0	8.0	10.0	6165	605
20						
8	4.0	1.0	7.0	8.5	6967	683
9	2.0	4.0	8.5	9.5	4710	462
10	3.0	3.0	11.0	12.0	5582	547
25						
11	4.0	2.0	8.5	10.5	5301	520
12	4.0	2.0	9.0	9.5	6197	608

As shown in Table I, the stiffness is higher when a greater proportion of the copolymer grease is used in place of the plasticizer. Cling, measured after 30 days aging, is also higher where a higher percentage of the copolymer grease and plasticizer blend is used. A stiffer film with higher cling is particularly advantageous for household film in that the film is less likely to tangle, tears easier from the roll, holds better to itself for sealing and gives a feeling of strength to the user. The copolymer grease/plasticizer blend mixes well and acts as an extrusion aid. It does not require operating conditions which significantly effect the degradation (color) of the vinylidene chloride copolymer resin.

It was also found that residual vinyl chloride and vinylidene chloride monomer levels were significantly lowered by use of the in-monomer addition of the grease copolymer without conventional plasticizer as compared with traditionally plasticized resins. The following Table II demonstrates the residual monomer data found. Control Run 1 was made with the traditionally plasticized vinylidene chloride copolymer resins, the other runs with the same vinylidene chloride copolymer resin only using the in-monomer addition of the grease copolymer as contemplated by the present invention in place of the plasticizer.

TABLE II
Residual monomer data (dried resin)

Run No.	Residual vinyl chloride	Residual vinylidene chloride
1-Control	0.1 ppm	47.0 ppm
2	10.4 ppb	2.0 ppm
3	58.0 ppb	*
4	10.0 ppb	*
5	<3 ppb	*
6	<3 ppb	*
7	<3 ppb	*

ppm=parts per million

ppb=parts per billion

* No data available.

The grease copolymer used in the present invention is highly viscous and customarily of a sticky nature making it an inconvenient material to handle and clean from machinery components. Such processing and handling is greatly enhanced by the addition of a conventional plasticizer.

5 Claims

1. A high cling film comprising an extrudable resin composition comprising:
 - (a) a vinylidene chloride copolymer in which a major proportion of the copolymer is vinylidene chloride monomer and a minor proportion of the copolymer is at least one other comonomer, and
 - (b) less than 10 percent by weight of total resin composition of a polymer blend consisting of a grease copolymer having a peak molecular weight of from 500 to 7500 as determined by gel permeation chromatography and a non-polymeric ester plasticizer.
2. The film of Claim 1, wherein the vinylidene chloride copolymer comprises from 70 to 95% by weight of vinylidene chloride with the remainder comprising one or more ethylenically unsaturated comonomers.
3. The film of Claim 1 or 2 wherein the grease copolymer and plasticizer blend comprises from 3.0 to 7.0% by weight of the total film composition.
4. The film of Claim 1, 2 or 3 wherein the grease copolymer comprises an ethylene and vinyl acetate copolymer resin, and the proportion of vinyl acetate is from 10 to 55 weight % of the grease copolymer and the peak molecular weight is within the range of from 1000 to 4000 as determined by gel permeation chromatography.
5. The film of any of the preceding claims, wherein the grease copolymer has a melt flow rate in the range of from 5 to 50 dg/min at a temperature of 80°C when conducted in accordance with the procedure of ASTM D-1238-70 (E) except that the diameter of the plastometer orifice is reduced to 0.50 ± 0.005 mm and the test temperature is 80°C.
6. The film of any of the preceding claims, wherein the ratio of grease copolymer to plasticizer is in the range of from 4:1 to 1:4.
7. The film of any of the preceding claims having a cling value of at least 5 grams as measured by a 30-day cling test and a stiffness in excess of 5300 kg/cm² after 15 days aging as defined by a 2% Secant Modulus test.
8. The film of any of the preceding claims, having a thickness of from 0.0051 mm to 0.076 mm.
9. The film of claim 8, having a thickness of from 0.0102 mm to 0.0254 mm.
10. A method of preparing an extrudable vinylidene chloride copolymer composition for films having a high-cling and reduced vinylidene chloride and/or vinyl chloride residuals and the vinylidene chloride copolymer is a copolymer in which a major proportion of the copolymer is vinylidene chloride monomer and a minor proportion of at least one other comonomer, the process comprising the step of adding to the composition prior to the polymerization less than 10 percent by weight of total resin composition of a polymer blend consisting of a grease copolymer having a peak molecular weight within the range of from 500 to 7500 as determined by gel permeation chromatography, and a conventional plasticizer and polymerizing the copolymer composition with the in-monomer grease copolymer and a non-polymeric ester plasticizer blend addition.

Patentansprüche

1. Stark haftender Film enthaltend eine extrudierbare Harzzusammensetzung enthaltend:
 - (a) ein Vinylidenchloridcopolymer in dem ein Hauptanteil des Copolymer Vinylidenchloridmonomer und ein kleiner Anteil des Copolymer mindestens ein anderes Comonomer ist und
 - (b) weniger als 10 Gew.% der Gesamtzusammensetzung einer Polymermischung bestehend aus einem Gleit-Copolymer mit einem durch Gelpermeationschromatographie bestimmten Peak-Molekulargewicht von 500 bis 7500 und einem nicht polymeren Esterweichmacher.
2. Film nach Anspruch 1, dadurch gekennzeichnet, daß das Vinylidenchloridcopolymer von 70 bis 95 Gew.% Vinylidenchlorid und ein oder mehrere ethylenisch ungesättigte Comonomere als verbleibenden Rest enthält.
3. Film nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Gleit-Copolymer- und Weichmachermischung von 3 bis 7 Gew.% der Gesamtfolienzusammensetzung beträgt.
4. Film nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß das Gleit-Copolymer ein Ethylen und Vinylacetat Copolymer Harz enthält und der Anteil von Vinylacetat im Gleit-Copolymer von 10 bis 55 Gew.% des Gleit-Copolymeren beträgt und das durch Gelpermeationschromatographie bestimmte Peak-Molekulargewicht im Bereich von 1000 bis 4000 liegt.
5. Film nach jedem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß das Gleit-Copolymer eine Schmelzflußgeschwindigkeit im Bereich von 5 bis 50 dg/min bei einer Temperatur von 80°C aufweist, wenn sie nach dem Verfahren nach ASTM D-12 38-70(E) bestimmt wird, mit der Abweichung, daß der Durchmesser der Plastometeröffnung auf $0.50 \pm 0,005$ mm verringert ist und die Prüftemperatur 80°C ist.
6. Film nach jedem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß das Verhältnis von Gleit-Copolymer zu Weichmacher im Bereich 4:1 bis 1:4 liegt.
7. Film nach jedem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß er einen Haftwert von

(13)

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2. The film of Claim 1, wherein the vinylidene chloride copolymer comprises from 70 to 95% by weight of vinylidene chloride with the remainder comprising one or more ethylenically unsaturated comonomers.
- 15 3. The film of Claim 1 or 2 wherein the grease copolymer and plasticizer blend comprises from 3.0 to 7.0% by weight of the total film composition.
4. The film of Claim 1, 2 or 3 wherein the grease copolymer comprises an ethylene and vinyl acetate copolymer resin, and the proportion of vinyl acetate is from 10 to 55 weight % of the grease copolymer and the peak molecular weight is within the range of from 1000 to 4000 as determined by gel permeation chromatography.
- 20 5. The film of any of the preceding claims, wherein the grease copolymer has a melt flow rate in the range of from 5 to 50 dg/min at a temperature of 80°C when conducted in accordance with the procedure of ASTM D-1238-70 (E) except that the diameter of the plastometer orifice is reduced to 0.50 ± 0.005 mm and the test temperature is 80°C.
- 25 6. The film of any of the preceding claims, wherein the ratio of grease copolymer to plasticizer is in the range of from 4:1 to 1:4.
7. The film of any of the preceding claims having a cling value of at least 5 grams as measured by a 30-day cling test and a stiffness in excess of 5300 kg/cm² after 15 days aging as defined by a 2% Secant Modulus test.
- 30 8. The film of any of the preceding claims, having a thickness of from 0.0051 mm to 0.076 mm.
9. The film of claim 8, having a thickness of from 0.0102 mm to 0.0254 mm.
10. A method of preparing an extrudable vinylidene chloride copolymer composition for films having a high-cling and reduced vinylidene chloride and/or vinyl chloride residuals and the vinylidene chloride copolymer is a copolymer in which a major proportion of the copolymer is vinylidene chloride monomer and a minor proportion of at least one other comonomer, the process comprising the step of adding to the composition prior to the polymerization less than 10 percent by weight of total resin composition of a polymer blend consisting of a grease copolymer having a peak molecular weight within the range of from 500 to 7500 as determined by gel permeation chromatography, and a conventional plasticizer and polymerizing the copolymer composition with the in-monomer grease copolymer and a non-polymeric ester plasticizer blend addition.
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 - (b) weniger als 10 Gew.% der Gesamtzusammensetzung einer Polymermischung bestehend aus einem Gleit-Copolymer mit einem durch Gelpermeationschromatographie bestimmten Peak-Molekulargewicht von 500 bis 7500 und einem nicht polymeren Esterweichmacher.
- 50 2. Film nach Anspruch 1, dadurch gekennzeichnet, daß das Vinylidenchloridcopolymer von 70 bis 95 Gew.% Vinylidenchlorid und ein oder mehrere ethylenisch ungesättigte Comonomere als verbleibenden Rest enthält.
3. Film nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Gleit-Copolymer- und Weichmachermischung von 3 bis 7 Gew.% der Gesamtfolienzusammensetzung beträgt.
- 55 4. Film nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß das Gleit-Copolymer ein Ethylen und Vinylacetat Copolymer Harz enthält und der Anteil von Vinylacetat im Gleit-Copolymer von 10 bis 55 Gew.% des Gleit-Copolymeren beträgt und das durch Gelpermeationschromatographie bestimmte Peak-Molekulargewicht im Bereich von 1000 bis 4000 liegt.
5. Film nach jedem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß das Gleit-Copolymer eine Schmelzflußgeschwindigkeit im Bereich von 5 bis 50 dg/min bei einer Temperatur von 80°C aufweist, wenn sie nach dem Verfahren nach ASTM D-12 38-70(E) bestimmt wird, mit der Abweichung, daß der Durchmesser der Plastometeröffnung auf 0.50 ± 0.005 mm verringert ist und die Prüftemperatur 80°C ist.
6. Film nach jedem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß das Verhältnis von Gleit-Copolymer zu Weichmacher im Bereich 4:1 bis 1:4 liegt.
- 65 7. Film nach jedem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß er einen Haftwert von



mindestens 5 Gramm, bestimmt durch einen 30 Tage-Haftungstest und eine Steifigkeit über 5300 kg/cm² nach 15 Tagen Alterung, bestimmt durch eine 2% Sekanten Modul-Prüfung aufweist.

8. Film nach jedem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß er eine Dicke von 0,00051 mm bis 0,076 mm aufweist.

5 9. Film nach Anspruch 8, dadurch gekennzeichnet, daß er eine Dicke von 0,0102 mm bis 0,0254 mm aufweist.

10. Verfahren zum Herstellen einer extrudierbaren Vinylidenchloridcopolymerzusammensetzung für Filme mit starker Haftung und verringerten Vinylidenchlorid und/oder Vinylchlorid-Rückständen und das Vinylidenchloridcopolymer ein Copolymer mit einem Hauptanteil Vinylidenchloridmonomer und einem
10 kleinen Anteil von mindestens einem anderen Comonomer des Copolymeren ist, wobei das Verfahren die Schritte enthält, Zugeben von weniger als 10 Gew.% der Gesamtharzzusammensetzung einer Polymermischung bestehend aus einem Gleitcopolymer mit einem durch Gelpermeationschromatographie bestimmten Peak-Molekulargewicht im Bereich von 500 bis 7500 und einem konventionellen Weichmacher der Zusammensetzung vor der Polymerisation und Polymerisieren der Copolymer-Zusammensetzung mit
15 der zugesetzten Mischung monomeren Gleit-Copolymeren und nicht polymerem Esterweichmacher.

Revendications

1. Film possédant une grande adhésivité qui comprend une composition de résine extrudable
20 comprenant:

(a) un copolymère de chlorure de vinylidène dans lequel une plus grande proportion de copolymère est le monomère de chlorure de vinylidène et une plus petite proportion de copolymère est au moins un autre comonomère, et

(b) moins de 10 pour cent en poids de la composition totale de résine d'un mélange de polymère
25 constitué d'un copolymère gras possédant une masse moléculaire avec un pic allant de 500 à 7500, celle-ci étant déterminée par chromatographie par perméation de gel et d'un plastifiant ester non polymère.

2. Film selon la revendication 1, caractérisé en ce que le copolymère de chlorure de vinylidène comprend de 70 à 95% en poids de chlorure de vinylidène, le reste comprenant un ou plusieurs comonomères à insaturation éthylénique.

30 3. Film selon la revendication 1 ou 2, caractérisé en ce que le mélange du plastifiant et du copolymère gras représente de 3,0 à 7,0% en poids de la composition totale du film.

4. Film selon l'une quelconque des revendications 1, 2 ou 3, caractérisé en ce que le copolymère gras comprend une résine de copolymère éthylène-acétate de vinyle, en ce que la proportion de l'acétate de vinyle est de 10 à 55% en poids du copolymère gras et en ce que le pic de masse moléculaire est compris
35 dans un intervalle allant de 1000 à 4000, celle-ci étant déterminée par chromatographie par perméation de gel.

5. Film selon l'une quelconque des revendications précédentes, caractérisé en ce que le copolymère gras possède une vitesse d'écoulement à l'état fondu comprise dans la gamme allant de 5 à 50 dg/min à une température de 80°C, ceci étant effectué conformément à la procédure de ASTM D-1238-70 (E) si ce
40 n'est que le diamètre de l'orifice du plastomètre est réduit à 0,50±0,005 mm et que la température de l'essai est de 80°C.

6. Film selon l'une quelconque des revendications précédentes, caractérisé en ce que le rapport du copolymère gras au plastifiant est compris dans l'intervalle allant de 4:1 à 1:4.

7. Film selon l'une quelconque des revendications précédentes qui possède une valeur d'adhésivité
45 d'au moins 5 grammes, celle-ci étant mesurée selon un essai d'adhésivité à 30 jours, et une rigidité dépassant 5300 kg/cm² après 15 jours de vieillissement, celle-ci étant définie par un essai du Module Secant à 2%.

8. Film selon l'une quelconque des revendications précédentes qui possède une épaisseur allant de 0,0051 mm à 0,076 mm.

50 9. Film selon la revendication 8 qui possède une épaisseur allant de 0,0102 mm à 0,0254 mm.

10. Procédé de préparation d'une composition extrudable de copolymère de chlorure de vinylidène pour films possédant une grande adhésivité et des taux réduits de chlorure de vinylidène et/ou de chlorure de vinyle résiduels, le copolymère de chlorure de vinylidène étant un copolymère dans lequel une plus grande proportion de copolymère est le monomère chlorure de vinylidène et une plus petite proportion de
55 copolymère est au moins un autre comonomère, ce procédé comprenant les étapes d'addition, à la composition avant la polymérisation, de moins de 10 pour cent en poids de la composition totale de résine d'un mélange de polymère constitué d'un copolymère gras possédant une masse moléculaire avec un pic allant de 500 à 7500, celle-ci étant déterminée par chromatographie par perméation de gel, et d'un plastifiant conventionnel, et de polymérisation de la composition de copolymère avec l'addition du
60 mélange d'un plastifiant ester non polymère et du copolymère gras dans le monomère.

