

Description

This invention is concerned with poly(vinyl chloride) compositions, especially those suitable for injection moulding, and to novel additives which modify their rheological properties.

It is known that processing of rigid "poly(vinyl chloride)" [otherwise PVC; by both of which terms we mean polymers containing at least 80 weight percent vinyl chloride units and we include chlorinated poly(vinyl chloride) and containing little or no plasticizer] is extremely difficult to accomplish without the use of polymeric processing aids. Such processing aids, when used at levels of from about 0.1 to about 10 parts per 100 parts of PVC, more usually from about 0.5 to about 10 phr (parts per 100 parts of PVC), cause the PVC to flux under heat into a thermoplastic leathery state on a mill roll or other similar mixer. The processing aids further allow the PVC to be processed in an extruder into a molten thermoplastic state without the need for high shear forces and temperatures. They further impart to the processed product smoother, uniform surfaces.

A thorough description of processing aids for PVC may be found in "Thermoplastic Polymer Additives, Theory and Practice," Edited by John T. Lutz, Jr., Marcel Dekker, Inc., New York and Basel, 1988 (chapter by R.P. Petrich and John T. Lutz, Jr.) and "History of Polymer Composites," Edited by R.B. Seymour and R.D. Deanin, VNU Science Press BV, Netherlands, 1987 (chapter by D.L. Dunkelberger).

Particularly useful as processing aids have been high molecular weight polymers which are predominately composed of units derived from methyl methacrylate and which have been commercially available for about 30 years. These additives are especially useful in that they do not detract from the important physical properties expected from the final processed PVC object, such as heat distortion temperature, tensile strength, and impact-resistance properties.

One deficiency that the commercially available acrylic processing aids of commerce have is that the high molecular weight polymers, even at the low levels used, either maintain or increase the melt viscosity of the resultant blend. This is especially undesirable in injection moulding applications, where it is desired to have a melt of low viscosity for ease in mould-filling. Lowering of the molecular weight of the processing aid will decrease the melt viscosity of the blend, but sometimes at the sacrifice of the heat distortion temperature of the final processed object.

Similar effects, i.e., improved flow at the expense of lowered heat distortion temperature, are found with other non-polymeric additives, such as plasticizers, or when a lower molecular weight PVC or a PVC copolymer is used.

Several polymeric additives based on polymers of (meth)acrylate esters have been disclosed as flow improvers for PVC. Simple homopolymers and copolymers, although effective, may delay fusion of the PVC; which is undesirable for rapid processing of the blend and for avoidance of overheating of the blend. Further, such single-stage materials are generally soft, difficult to isolate from their preparative media, and difficult to blend with the PVC. Further, when the additive is immiscible with the PVC and of significantly differing melt viscosity at processing temperatures, orientation effects may be seen in injection moulding, and delamination of the processed blend may occur.

Multistage structures, often known as core-shell polymers, usually specifically described as graft polymers, have been described as useful for this purpose. However, the combination of relatively high molecular weight for the various stages and the chemical combination of the stages (grafting) make such materials less suitable for flow improvement in PVC formulations based on low molecular weight PVC, such as those of potentially commercial interest for injection moulding. Further, when the molecular weight of the first stage is decreased and the compatibility with the PVC lessened to produce an additive which does not increase the melt viscosity of the blend with PVC, then delay of fusion is noted.

There has thus been a long-felt need for an additive which will allow PVC to be processed in injection moulding to useful objects which maintain the physical properties of a medium- to high-molecular weight PVC, such as heat distortion temperature and toughness, while being capable of being moulded under commercially practical and safe conditions of temperature, time, and pressure, which will further produce uniform, non-delaminated blends with PVC, which does not detract from, and preferentially enhances, the impact strength of the PVC blend, and which produces minimal deleterious effects on the fusion properties of the blend.

We have discovered that an appropriate non-crosslinked higher alkyl (i.e. from four to twelve carbon atoms in the alkyl group), (meth)acrylate ester initial-stage, usually first-stage polymer capable of functioning as an additive to reduce viscosity in PVC blends can better achieve these desired properties by encapsulating the first stage or core polymer by an appropriately crosslinked subsequent polymer, usually second polymer, (shell). In our invention, the second polymer is crosslinked by physical and optionally, chemical bonds. It is important that the first stage polymer not be deliberately crosslinked, such as by a

post-cure or vulcanization with, e.g., peroxide, or by incorporation of multifunctional monomers such as divinylbenzene or ethylene glycol dimethacrylate, so that multi-functional monomers should be avoided in its polymerization. Preparative conditions, such as polymerization at temperatures below about 60 degrees C., should be chosen which are known to those skilled in the art to decrease crosslinking. Preferably the molecular weight should be controlled (decreased), by means such as use of a chain-transfer agent, so as to avoid inadvertent crosslinking known to be common in higher alkyl acrylate ester polymerizations in emulsion.

The encapsulating shell polymer serves several functions in improving the utility of the core/shell polymer as an additive for injection moulding of PVC. Especially when it is a polymer having a glass temperature higher than that of the core, the shell aids in isolation of the core/shell polymer, and in handling the core/shell polymer during addition to the PVC for blending. Especially if the subsequent shell polymer is a rubbery polymer, such as a polymer rich in units derived from butyl acrylate, the presence of the shell polymer toughens the resulting PVC blend more effectively than the core polymer alone.

A further stage or stages may be present, providing outer shell polymer, which may, for example, serve as a compatibilizing aid with PVC, or as a processing aid to promote fusion. Structurally similar but different core shell polymers used as impact modifiers for polymethylmethacrylate or polystyrene, are disclosed in international patent application WO-A-8805450.

According to the invention, the additive structure is a core/shell polymer comprising:

(a) a core of polymer containing at least about 80 weight percent of units derived from a higher alkyl (meth)acrylate, the higher alkyl group containing from four to twelve carbon atoms, such as butyl acrylate, 2-ethylhexyl acrylate, octyl methacrylate, and the like, the core polymer not containing units derived from a graftlinking or crosslinking monomer, and the core polymer being substantially non-crosslinked, where preferably the weight average molecular weight of the core polymer is from 5000 to 100,000;

(b) a shell stage of crosslinked polymer, the crosslinked polymer containing:

(i) at least about 90 weight percent of units derived from one or more vinyl aromatic monomers, such as styrene or vinyl toluene, or alkyl esters of (meth)acrylic acid, wherein the alkyl esters are derived from alcohols of from one to four carbon atoms, such as methyl methacrylate, ethyl methacrylate, methyl acrylate or butyl acrylate;

(ii) from about 0.5 to about 10 weight percent of units derived from at least one of:

a) copolymerisable unsaturated acid of which from 10 to 100% by weight are in the form of an alkali, alkaline earth or transition metal salt; and, optionally

b) multifunctional monomer containing two or more copolymerizable double bonds, such as divinylbenzene, butylene glycol dimethacrylate, butylene glycol diacrylate, allyl methacrylate or diallyl maleate.

The core/shell polymer may further comprise a final shell stage of polymer containing at least about 70 weight percent of units derived from one or more of vinyl aromatic monomers or lower alkyl esters of methacrylic acid, wherein the lower alkyl esters are derived from alcohols of from one to four carbon atoms. Preferred are the compositions wherein the higher alkyl(meth)acrylate is n-butyl acrylate and the lower alkyl ester of methacrylic acid of the final shell stage is the methyl ester. For best impact properties, it is preferred that the monomer in the shell stage be butyl acrylate.

The unsaturated acid and/or its alkali, alkaline earth or transition metal salt must be copolymerizable with the alkyl (meth)acrylate or vinyl aromatic. "Alkali metal" encompasses sodium, potassium, lithium, cesium, and rubidium, of which sodium and potassium are preferred. "Alkaline earth metal" encompasses calcium, magnesium, strontium, and barium, of which calcium and magnesium are preferred. "Transition metal" encompasses chromium, manganese, iron, cobalt, nickel, copper, zinc, zirconium, molybdenum, cadmium, lanthanum, tungsten, and mercury, of which zinc is preferred.

The acid groups may be derived by partial hydrolysis or pyrolysis of a blocked acid group, such as hydrolysis of a methyl ester or pyrolysis of a tertiary-butyl ester. However, it is most convenient to incorporate them by copolymerization of a suitable unsaturated acid-containing monomer, which is copolymerized as the unsaturated acid and then post-treated to form the salt, or alternatively may be copolymerized directly as the salt. The unsaturation is preferably conjugated with the acid group, such as with methacrylic acid, monoethyl maleate, and the like, but may be remote from the acid group if the copolymerization proceeds readily, such as with p-vinylbenzenesulfonic acid or acryloxypropionic acid. The unsaturated acid may be a sulfonic acid, such as styrenesulfonic acid, a partially esterified sulfuric acid, such as beta-sulfatoethyl methacrylate, a phosphonic acid, such as styrenephosphonic acid, a phosphoric acid, such as beta-phosphatoethyl acrylate, and the like. Preferred for ease of incorporation and availability are unsaturated carboxylic acids, or their immediate, readily available precursors, such as unsaturated

anhydrides. Included are such monomers as acrylic acid, methacrylic acid, alpha-phenylacrylic acid, itaconic acid, maleic acid, fumaric acid, monoalkyl fumaric acid, methacrylic acid, acrylic acid, crotonic acid, alpha-methylene-delta-methyladipic acid, acryloxypropionic acid, p-vinylbenzoic acid, monovinyladipic acid and maleic anhydride. Especially preferred, for retention of glass temperature of the blend, availability, and ease of incorporation, is methacrylic acid. Total neutralization of the units derived from the copolymerized unsaturated acid is not necessary. As above stated at least 10% up to 100% are neutralized.

It is preferred that the said final outer shell be included, and that it should be at least 10 weight percent of the final polymeric composition, preferably from 15 to 25 weight percent. That amount will aid in isolation of the additive, promote its free powder flow, yet not dilute too much the efficacy of the flow aid portion. The amount of the crosslinked stage should be from 10 to 50 parts of the total composition, preferably from 20 to 40 weight percent.

The invention further provides blended compositions comprising polymer of vinyl chloride and additive polymers as described above. The major utility of such blends will be when the blend composition has a melt viscosity, as measured under injection-moulding conditions, equal to or less than the melt viscosity for the polymer of vinyl chloride without the additive polymer. The polymer of vinyl chloride may be a homopolymer of vinyl chloride, or a copolymer containing at least about 80 weight percent vinyl chloride units and up to about 20 weight percent of units derived from one or more other copolymerisable monomer, especially propylene, ethylene, vinyl acetate, vinylidene chloride and/or lower alkyl acrylate units. Preferred for injection moulding purposes are polymers of vinyl chloride having a weight-average molecular weight of from 40,000 to 120,000, or a Fikentscher K value of from 50 to 60.

Further, we include, within the term "polymer of vinyl chloride", chlorinated poly(vinyl chloride), which also will demonstrate improved processability when admixed with the additive polymers of the present invention.

For most uses, however, where exposure to heat may occur, it is preferred to use a homopolymer of vinyl chloride or a copolymer with a monomer whose homopolymer has a high glass temperature, such as styrene, alpha-methylstyrene, a maleimide, so as to obtain the highest value of heat distortion temperature for the blend. Especially preferred for cost and availability is the homopolymer of vinyl chloride. The polymers of vinyl chloride may be prepared by any of the known means; preferred are bulk and suspension polymerization.

The blended composition will preferably contain from 2 to 15 parts of the additive polymer per 100 parts of the polymer of vinyl chloride. The blend will preferably exhibit an immiscible or partly immiscible morphology at injection moulding conditions, at least the core or first-stage component of the additive polymer being at least partially immiscible in the PVC matrix.

The additive polymer may be isolated from its preparative media by filtration and washing, if the polymer is insoluble in the media. If soluble, a precipitant may be added, the polymer filtered, washed, and dried. If the additive polymer is in the form of a non-aqueous dispersion, the solvent may be evaporated, and the polymer comminuted to powder. If the polymeric additive is formed in aqueous dispersion, it may be isolated by evaporation, by coagulation, or by spray-drying. This isolation may be accomplished in the presence of the PVC; for example, the aqueous dispersion may be evaporated onto the PVC and the mixture dried prior to addition of other additives and blending. Another method is to co-isolate aqueous dispersions of the PVC and the polymeric additive. Since PVC itself requires adjuvants for processing and/or improvement of its physical properties, the blend will preferably further contain one or more of impact modifier, lubricant, thermal stabilizer, plasticizer, surface-altering agent, organic pigment, heat-distortion improver additive, organic dye, or mould release agent. The PVC/additive blend may further contain one or more inorganic or organic filler or fibre.

The invention further encompasses film, sheet, extruded or moulded articles, especially injection-moulded articles, formed from the blend of PVC and the additive polymer.

The amount of the additive polymer of the present invention will vary depending on the processing conditions chosen and the molecular weight of the PVC resin used. For most uses, the blend will contain from 1 to 20 parts of the additive polymer per 100 parts of the polymer of vinyl chloride, but higher or lower levels may be employed in certain circumstances. Preferred for the best balance of efficacy without detracting from the physical properties of the blends is from 2 to 15 parts of the additive polymer.

For injection moulding purposes, it is preferred that the additive polymer be partially or totally immiscible with the polymer of vinyl chloride during the injection moulding process. The additive polymer and the polymer of vinyl chloride will exhibit an immiscible morphology at least in the molten state of the injection moulding process, and possibly even when the melt is cooled. An immiscible morphology will exhibit itself in a lowering of transparency or a detection of one or more phases by microscopy or a detection of more than one glass temperature by, e.g., differential scanning calorimetry. A partially

immiscible morphology will exhibit itself in a similar manner, but the glass temperatures may not be those of the corresponding phases when measured separately, but instead some dilution or modification of the value will be noted.

The additive polymer need not function as a processing aid per se (that is to say that it need not necessarily cause the PVC to flux or melt more readily and quickly to convert to a fluid elastoplastic) as long as it functions to reduce the melt viscosity of the blend without adversely affecting other key properties. It may then be necessary to add a small amount of a conventional processing aid for PVC to aid in fluxing and processing the blend. Preferred is the case where the final shell polymer also functions as a processing aid.

So as not adversely to affect the flow of the blend upon processing, it is preferred that the weight-average molecular weight of any other stage of the multi-stage additive be below about 100,000. To exhibit the best efficiency, it is preferred that just enough of any other stage of the multi-stage polymer be present to aid in isolation, so that at least 50% weight percent of the multi-stage polymer, and preferably at least 70% of the multi-stage polymer, is the additive component.

For ease in dispersing the acrylic core stage, it is preferred that at least one stage, such as the final outer shell, of the multi-stage additive be miscible with the polymer of vinyl chloride, such as being a polymer formed predominantly of units derived from methyl methacrylate.

The polymeric additive is normally added to the poly(vinyl chloride) by dry-blending prior to processing. At the same time, other ingredients usual in the art and necessary to processing the PVC without thermal decomposition may be added. Such stabilizers may be organotin compounds, such as dimethyl dilisoctylthioglycolate, calcium-zinc salts of organic acids, such as calcium stearate or zinc stearate or their mixtures, organolead compounds, such as dibasic lead phosphite, organocadmium and organobarium compounds, and the like. Such stabilizers are usually present at levels from about 0.1 to about 5 parts per 100 parts of PVC resin, conventionally noted as phr.

Other additives may be present in the dry-blend, such as pigments, such as infra-red adsorbing pigments, dyes, and the like; plasticizers; other processing aids or lubricants designed to improve fluxing of the mix or avoidance of sticking to hot metal surfaces, such as butyl acrylate/styrene/ / methyl methacrylate or butyl acrylate/ /methyl methacrylate core/shell polymers with a low molecular weight core and a high molecular weight shell; other lubricants, such as long chain fatty acids, their salts, and their long chain esters, low molecular weight polyolefins; flame retardants or smoke retardants, such as zinc oxide or organophosphorus compounds; ultraviolet stabilizers, such as hindered phenols, hindered amines and aromatic o-hydroxyketones; heat distortion improvers, such as polyglutarimides, copolymers of isobornyl methacrylate, copolymers of alpha-methylstyrene/methyl methacrylate/acrylonitrile or copolymers of styrene or alpha-methylstyrene with maleic anhydride and/or a maleimide; and other additives known to the art.

Also present may be impact modifiers, at amounts of from 3 to 20 phr. Many materials are known to be impact modifiers for PVC. Such include core/shell polymers of a butadiene-based core, such as poly-(butadiene), poly(butadiene-styrene), poly(butadiene-acrylonitrile), or poly(butadiene-butyl acrylate), with one or more shells of poly(methyl methacrylate), poly styrene, poly(styrene-acrylonitrile), poly(styrene-methyl methacrylate) or poly(styrene-methyl methacrylate-acrylonitrile). These core/shell polymers are efficient impact modifiers for non-weatherable applications.

Another useful class of impact modifiers are those based on poly(alkyl acrylates), such as core/shell modifiers with poly(butyl acrylate) cores, the butyl acrylate polymer being a homopolymer or a copolymer containing styrene, and further containing polyunsaturated monomers, such as divinylbenzene, glycol dimethacrylates, glycol diacrylates, polyol polymethacrylates or allyl methacrylate. The outer shell of such polymers is usually a polymer rich in units derived from methyl methacrylate or a copolymer of styrene with acrylonitrile.

Other classes of impact modifiers may also be employed, such as single- or multi-stage polymers based on an ethylene-propylene or ethylene-propylene-non-conjugated diene rubber, or a butadiene-acrylonitrile rubber, or a silicone-based elastomer, or a ethylene-vinyl acetate rubber, or chlorinated polyethylene.

There may further be present one or more of a variety of fillers, either reinforcing or non-reinforcing. Such fillers, which include fibrous, flaked, and powdery materials, will be present in amounts from 1 to 50 phr. They may contain chemical coupling agents, such as organotitanates or functionalized silicon additives, to aid in adhesion to the PVC. Such fillers include glass fibre, glass flakes, glass microspheres; other mineral fibres; talc, wollastonite, mica; carbon black; alumina, silica, titanium dioxide.

As noted, it is most common to combine all ingredients of the PVC blend prior to actual melt-processing, although additives may be added to the melt if desired. Normally the dry blend is then processed with heat and shear, such as in an intensive mixer, such as a Brabender or Banbury, on a two-

roll mill, or in an extruder, until the PVC has "fluxed" or passed to a molten form. The fluxed material may then be dropped from the mixers, or sheeted into forms suitable for compression moulding, or for re-melting and re-processing.

For most uses, the molten polymer is conveyed through an extruder, usually either a single-screw or double-screw extruder at temperatures and shear conditions sufficient to convey the molten material readily but without causing over-heating and degradation. The melt may then be passed through one or more dies into strands for pelletizing, with the pellets later be re-processed into the final desired article. On the other hand, the melt may be directly converted into the final object by such operations as passing through an appropriate die to form a sheet, film, or profile-shaped article. The melt may also be formed into parisons for subsequent blow-moulding. The melt may also be injection-moulded by injection into an appropriate mould to form moulded objects.

For the latter operation especially, the melt needs to be fluid to fill the mould rapidly and completely at as low a temperature and pressure of processing as possible. Otherwise, moulding will take longer or require more extreme conditions of temperature and pressure, which is both uneconomical and leading to polymer degradation.

Several means exist for measuring the effect of the additive on the flow behaviour of the PVC compound. One is to compare the extent of mould fill in a long spiral mould under similar pressure/temperature conditions versus a PVC compound absent the additive, or against commercially purchased PVC injection moulding blends. A second test is to measure pressure required to fill such a mould against such controls. A third is to measure a melt flow rate, extruding through a standardized orifice at standard conditions and measuring the amount of polymer extruded in 10 minutes versus such controls. A fourth is to compare viscosity values measured over a range of shear rates at a constant temperature in a commercial device for obtaining viscosity-shear rate response, such as a capillary rheometer. A fifth method is by comparing the value of equilibrium torque in a mixing device designed to measure torque at various temperatures of mixing as a value of time, such as certain rheometers.

Poly(vinyl chloride) containing the additives of the present invention may be converted into many useful forms. Injection-moulded PVC may be used to form many objects by direct injection moulding, that is, moulding into objects which require no further formation, such as stretching, blowing, etc., for consumer use. Such objects include toys, novelty items, automobile interior parts, such as trim knobs, door latches and lock handles, connectors, seat belt latch covers, ashtrays, fuse boxes, other automotive uses, such as bumpers, wheel wells, liners, parts for under-the-hood use, such as windshield washer and other aqueous fluid reservoirs, electrical connections, medical products, such as syringes and stoppers, appliance parts, such as lint filter housings for washing machines, spin tubs or agitators for washing machines, pump components, blower wheels, insulators, fan protective grills, switch housings, handles, household uses, such as bowls, cups, containers, covers for containers, such as coffee can lids, boxes for packaging of film, tape, disks, components of such recording devices, such as cassettes, film spindles, packaging uses, such as automotive dunnage, trays, tool handles, electrical plugs, pails, tubs, waste containers, laundry baskets, bottle base cups, paint cans, closures, such as for carbonated beverage containers, parts for appliances, such as refrigerator crispers, door liners, and many other similar forms.

Blow-moulding may also be utilized to form useful objects by forming an extruded- or injection moulded parison, then inflating and forming the parison in to the desired shape. Thus, bottles and other containers, and many other similar objects, may be prepared. The PVC compound containing the additive may also contain a chemical blowing agent, which will decompose at a higher temperature of processing to release a gas for causing the molten PVC to form foam, maintaining enough melt strength to retain the foamed shape on cooling. A gas may also be injected into the melt to form the foam.

The PVC compound containing the additive may be employed in the manufacture of many useful objects in profile form, such as clips, scrapers, luggage beads, garden edging, door stripping, gutters, downspouts, corrugated roofing, window and door casings, window tracks, siding, rub/bruise strips, such as for cars and appliances, coated wire, picture framing, pipe for drain, waste, or vent use, electrical conduit, ducts, sheathings for wood, protective fascia, such as for automobiles, automotive liners, appliance components such as liners, hinges, edgings, trays, beam covers, straws for consuming drinks, troughs, corrugated tubing, support poles, such as for plants, ski poles. The additive polymer will also be useful in processing blends of PVC with other polymers with which it is compatible, such as acrylonitrile-butadiene-styrene resins, and the like.

EXAMPLES: The following examples describe the synthesis of the additives and the testing of the additives in a PVC formulation for flow, impact, and heat distortion effects. BA = n-butyl acrylate; MMA = methyl methacrylate; ALMA = allyl methacrylate; n-DDM = n-dodecyl mercaptan.

A. Preparation of Multistage Flow Improving AdditivesExample 1

This example describes the preparation of a core/shell additive with both ionic and covalent crosslinking of the intermediate state, and the neutralization of the methacrylic acid component to form the monomer. The structure is 50.5 BA(n-DDM)/34.5 BA(ALMA)/(MAA)/15MMA(n-DDM) 100/(1%)/100/ (0.6%)/(3%) //100 (0.8)

Stage I -- Uncrosslinked polybutyl acrylate

In a glass reactor, 663 g deionized water and 20 g of 2 wt.% acetic acid are mixed and heated to 55 °C. Nitrogen gas is bubbled through this solution for at least 20 minutes. At 55 °C under a continuous nitrogen sweep, 1.07 g 28% sodium lauryl sulfate aqueous solution diluted with 10 g water are added to the flask. Then a mixture of 100 g n-butyl acrylate and 1 g n-dodecyl mercaptan is added to the flask followed by 50 g rinse water. After the mixture is stirred for 2 minutes, 80 g of 5% sodium formaldehyde sulfoxylate aqueous solution and 28 g of 5% t-butyl hydroperoxide aqueous solution are charged to the flask. An exotherm of 12-14 °C is observed. After reaching the peak temperature, a pre-emulsified monomer mixture containing 700 g water, 56.07 g 28% sodium lauryl sulfate solution, 1900 g n-butyl acrylate and 19 g n-dodecyl mercaptan are introduced into the reactor gradually in three hours. At the same time, 180 g 5% t-butyl hydroperoxide aqueous solution are also added in three hours. At the beginning of the three hours and in the middle of the three hours, 40 g of 5% sodium formaldehyde sulfoxylate solution are added to the reaction mixture (total of 80 g). When the gradual feed is complete, a temperature of 78 - 80 °C is usually achieved. The monomer emulsion container is rinsed with 200 g water and this rinse water is charged to the reactor. Fifteen minutes after the feed, 16 g of 5% sodium formaldehyde sulfoxylate solution and 8 g of 5% t-butyl hydroperoxide solution are added to the reactor. The mixture is allowed to cool to room temperature. The solids content of this final emulsion is 49.6% and the polymerization conversion is 99.2%; the molecular weight is 64,000 (Mw).

Stage II -- Encapsulating polymer stage

A mixture of 1966 g Stage I emulsion, 698 g water and 26.8 g of 28% sodium lauryl sulfate solution is heated to 55 °C under nitrogen sweep. In 80 minutes, a monomer mixture containing 636.6 g n-butyl acrylate, 19.14 g methacrylic acid and 3.90 g allyl methacrylate is gradually added to the reactor. At the same time, 52.3 g of 5% t-butyl hydroperoxide aqueous solution are also gradually added in 80 minutes. Two additions of 26.2 g 5% sodium formaldehyde sulfoxylate solution each are added to the reactor at the beginning and in the middle of the gradual feed period. The temperature at the end reaches 68 °C. 50 g water are used to rinse the monomer container and the rinse water is added to the reactor afterwards. After a 30 minute hold at a temperature of 60 °C, 99.8% conversion is achieved.

Stage III -- Final outer stage

The Stage II emulsion described above is cooled to 55 °C. Then a solution of 12.2 g 5% sodium formaldehyde sulfoxylate is added. A mixture of 287.6 g methyl methacrylate and 2.29 g n-dodecyl mercaptan is added to the reaction mixture in 30 minutes and 12.2 g 5% t-butyl hydroperoxide solution are also added in 30 minutes. At the end of the gradual addition, the mixture is held at 60 °C for 15 minutes. Polymerization of the residual monomer is completed by an addition of 2.4 g 5% t-butyl hydroperoxide solution and 2.4 g 5% sodium formaldehyde sulfoxylate solution. The final emulsion has a solids content of 49.7% and a conversion of 99.5%.

Neutralization of Example 1

To 3624 g of the final emulsion, 167.2 g 5% sodium hydroxide aqueous solution and 559 g water are added under stirring. The mixture is stirred at room temperature for 18 hours. The final pH of the emulsion is 10.1.

Coagulation of Example 1

3863 g of the neutralized emulsion are diluted with 2147 g water. The emulsion is then gradually poured into 10667 g 0.475% calcium chloride aqueous solution at 5 °C. The coagulated latex is isolated by filtration followed by washing with 4800 g water. The powder is dried in a 50 ° vacuum oven.

Example 2

This example describes a three-stage core/shell additive of the structure 50.5 BA/St/n-DDM//34.5 BA/(MAA)/(ALMA)//15MMA/(n-DDM) 80/20 (1%)// 100/(3%)/(0.6%)// 100(0.8%).

Stage 1 - Uncrosslinked butyl acrylate/styrene copolymer

In a glass reactor, 663 g deionized water and 20 g of 2 wt.% acetic acid are mixed and heated to 55 °C. Nitrogen gas is bubbled through this solution for at least 20 minutes. At 55 °C under a continuous nitrogen sweep, 1.07 g 28% sodium lauryl sulfate aqueous solution diluted with 10 g water are added to the flask. Then a mixture of 80 g n-butyl acrylate, 20 g styrene and 1 g n-dodecyl mercaptan is added to the flask followed by 50 g rinse water. After the mixture is stirred for 2 minutes, 80 g of 5% sodium formaldehyde sulfoxylate aqueous solution and 28 g of 5% t-butyl hydroperoxide aqueous solution are charged to the flask. An exotherm of 12-14 °C is observed within 15 minutes. After reaching the peak temperature, a pre-emulsified monomer mixture containing 700 g water, 56.07 g 28% sodium lauryl sulfate solution, 1520 g n-butyl acrylate, 380 g styrene and 19 g n-dodecyl mercaptan is introduced into the reactor gradually in three hours. At the same time, 180 g 5% t-butyl hydroperoxide aqueous solution are also added in three hours. At the beginning of the three hours and in the middle of the three hours, 40 g of 5% sodium formaldehyde sulfoxylate solution are added to the reaction mixture (total of 80 g). When the gradual feed is complete, a temperature of 78 - 80 °C is usually achieved. The monomer emulsion container is rinsed with 200 g water and this rinse water is charged to the reactor. Fifteen minutes after the feed, 16 g of 5% sodium formaldehyde sulfoxylate solution and 8 g of 5% t-butyl hydroperoxide solution are added to the reactor. The mixture is allowed to cool to room temperature. The solids content of this final emulsion is 49.6% and the polymerization conversion is 99.2%.

Stage II-- Encapsulating polymer stage

A mixture of 1966 g Stage I emulsion, 698 g water, and 26.8 g of 28% sodium lauryl sulfate solution is heated to 55 °C under nitrogen sweep. In 80 minutes, a monomer mixture containing 636.6 g n-butyl acrylate, 19.14 g methacrylic acid, and 3.90 g allyl methacrylate is gradually added to the reactor. At the same time, 52.3 g of 5% t-butyl hydroperoxide aqueous solution are also gradually added in 80 minutes. Two additions of 26.2 g 5% sodium formaldehyde sulfoxylate solution each are added to the reactor at the beginning and in the middle of the gradual feed period. The temperature at the end reaches 68 °C. 50 g water are used to rinse the monomer container and are added to the reactor afterwards. After a 30 minute hold at temperature of 60 °C, 99.2% conversion is achieved.

Stage III -- Final outer stage

The Stage II emulsion described above is cooled to 55 °C. Then 12.2 g of 5% sodium formaldehyde sulfoxylate solution are added. A mixture of 287.6 g methyl methacrylate and 2.29 g n-dodecyl mercaptan is added to the reaction mixture in 30 minutes and 12.2 g of a 5% t-butyl hydroperoxide solution are also added in 30 minutes. At the end of the gradual addition, the mixture is held at 60 °C for 15 minutes. Polymerization of the residual monomer is completed by an addition of 2.4 g 5% t-butyl hydroperoxide solution and 2.4 g 5% sodium formaldehyde sulfoxylate solution. The final emulsion has a solids content of 49.7% and a conversion of 99.4%.

Neutralization of Example 2

To 3624 g of the final emulsion, 167.2 g of 5% sodium hydroxide aqueous solution are added under stirring. The mixture is stirred at room temperature for 18 hours. The final pH of the emulsion is 10.1.

Coagulation of Example 2

The neutralized emulsion is diluted with 2230 g water. The emulsion is then gradually poured into 12100 g 0.475% calcium chloride aqueous solution at 5°C. The coagulated latex is isolated by filtration followed by washing with 5000 g water. The powder is dried in a 50°C vacuum oven.

B. Processing Techniques for PVC/Multistage Additive Blends

1. Blending

The PVC injection moulding formulations were prepared by blending all of the formulation components except the flow improving additive in a 35-lb (15.9 kg) Henschel mixer. The formulation components are shown in Table 1. The blending procedure involves mixing the PVC resin alone in the high-intensity mixer until it shear heats to 52°C. The liquid organotin stabilizer is then added to the blend. The blend is allowed to shear heat to 66°C and the lubricants, glyceryl monostearate and a polyolefin wax, are added to the blend. The blend is allowed to shear heat to 77°C and the acrylic processing aid and the acrylic impact modifier are added. The blend is permitted to shear heat to 82°C and the TiO₂ is added. High intensity mixing is continued until the blend temperature reaches 95°C. The blend is then cooled with only slow stirring to 60°C by circulating water through the mixer jacket. The blend, which will be referred to as the PVC masterbatch, is removed from the mixer at approximately 60°C.

The blends containing flow improving additives are prepared by mixing the desired amounts of PVC masterbatch and flow improving additive together in a 5-lb high intensity blender at room temperature for five minutes (the blend temperature will exceed room temperature due to shear heating but no additional heat is applied).

Table 1

PVC Injection Moulding Formulation

100.0 phr PVC (K=60) Resin
2.0 phr dimethyltin bis(2-ethylhexylthioglycolate)
2.7 phr glycerol monostearate
0.3 phr polyolefin wax - external lubricant
1.0 phr high Mw poly(MMA/EA) copolymer
8.0 phr core/shell BA/MMA copolymer
1.5 phr TiO ₂
0.4 or 8 phr Flow Improving Additive

2. Extruding and Pelletizing

The blends are extruded using an American Leistritz counter-rotating twin-screw extruder and pelletized. The extruder is equipped with 34 mm counter-rotating screws. There are five barrel sections giving a total length to diameter ratio of 15.9. The barrel temperatures are set at 140°/145°/150°/155°C (Note: no heat to first barrel) and the die temperature is set at 160°C. The blends are extruded into a single strand through a 1/8" diameter die and cooled by passing through a water bath before being chopped into pellets.

3. Injection Moulding

ASTM parts for impact testing are moulded using an ASTM parts cluster Master Unit Die insert in an Arburg 270-90-350 injection moulding machine. The injection moulding machine has a 22 mm diameter screw with a length to diameter ratio of 20.5 and a compression ratio of 2.1. The barrel temperatures are set at 146°, 171°, and 177°C and the nozzle temperature is set at 186°C. These settings produce a melt temperature of approximately 210°C as measured for an air shot using a hand-held pyrometer with needle probe. The mould temperature is 32°C. The screw speed is set at 200 rpm. An 1/8" (3.175 mm) thick Izod impact bar, a 1/4" (6.35 mm) thick Izod impact bar, and a 2" x 3" x 1/8" (50.8 mm x 76.2 mm x 3.175 mm) plaque for instrumented drop dart impact are moulded from each shot.

The spiral flow moulding was done using a spiral shape Master Unit Die insert in the same machine with the same barrel temperatures, mould temperature, and screw speed.

Example 3

Flow Improvement of PVC Blends Containing Multistage Flow Improving Additives

PVC formulation blends with 4 phr and 8 phr (phr = parts per hundred resin) of the flow improving additives are prepared according to the procedures described above. Spiral flow moulding is conducted to measure the flow effects of the additives. The additives are referred to as B, and C; B is prepared by the method of Example 1 and C by the method of Example 2. The spiral flow lengths are measured for three different injection pressures for each blend. The spiral flow data are compiled in Table 2. The spiral flow length values shown in the table correspond to the averages and standard deviations (in parentheses) based on sets of five measurements for each blend. These data show that the additives significantly increase the material flow in the injection mould.

Table 2

Spiral Flow Measurements				
Blend	Flow Improving Additive	Spiral Flow Length (cm) for Injection Pressure P		
		P = 476 bar	P = 714 bar	P = 1582 bar
1	None	10.52 (± 0.28)	16.97 (± 0.10)	44.45 (± 1.04)
2	4 phr B	10.72 (± 0.10)	17.27 (± 0.00)	47.22 (± 1.40)
3	4 phr C	11.23 (± 0.10)	17.68 (± 0.13)	47.19 (± 1.09)
4	8 phr B	13.46 (± 0.48)	21.95 (± 0.13)	56.79 (± 0.13)
5	8 phr C	15.75 (± 0.30)	23.83 (± 0.33)	59.18 (± 0.25)

Example 4

Impact Properties of PVC Blends Containing Multistage Flow Improving Additives

PVC formulation blends are prepared with 8 phr of the flow improving additives B, and C (corresponding to Examples 1 and 2 respectively) according to the procedures described previously. 1/8" (3.175 mm) thick and 1/4" (6.35 mm) thick Izod bars are injection moulded. The notched Izod impact properties of these moulded bars are tested according to ASTM Standard D256. Test temperatures of 15°C, 18°C, and 23°C are used for the 3.175mm (1/8") thick samples. Test temperatures of 18°C and 23°C are used for the 6.35 mm (1/4") thick samples. Impact measurements are made on five bars for each blend. The impact measurement averages for hinge and clean breaks are given in Tables 3 and 4. The numbers in parentheses represent the percentage of samples that break in each mode when more than one type of fracture is observed. The measurements show that the ductility of the blends is retained to lower temperatures for the blends containing the flow improving additives as compared with the PVC blend without the additives. The Izod impact strengths for brittle (complete) fractures are also increased for the blends containing the flow improving additives.

Table 3

Notched Izod Impact Measurements for 1/8" (3.175 mm) Thick Samples							
Blend	Flow Improving Additive	Notched Izod Impact Strength (J/m)					
		15 ° C		18 ° C		23 ° C	
		Hinge	Complete	Hinge	Complete	Hinge	Complete
1	None	--	70	--	161	1178	--
2	8 phr B	975 (60%)	179 (40%)	984	--	1092	--
3	8 phr C	--	197	904 (40%)	317 (60%)	947	--

Table 4

Notched Izod Impact Measurements for 1/4" (6.35 mm) Thick Samples					
Blend	Flow Improving Additive	Notched Izod Impact Strength (J/m)			
		18 ° C		23 ° C	
		Hinge	Complete	Hinge	Complete
1	None	--	86	--	94
2	8 phr B	916	--	945	--
3	8 phr C	839	--	905	--

Example 5**Vicat Softening Temperature Measurements**

One of the desired characteristics of the flow improving additives is that they not decrease the heat distortion temperature of the PVC formulation. Vicat softening temperatures are measured on 1/4" (6.35 mm) thick moulded bars for 1 and 5 kg loads at a heating rate of 120 °C/hr according to ASTM Standard D1525. The data are shown in Table 5. The values represent the average of two temperature readings for each sample. The data indicate that the additives do not have a significant effect on the 1 kg load Vicat temperature and only a small effect (~1 °C) on the 5 kg load Vicat temperature.

Table 5

Vicat Softening Temperatures for 1/4" (6.35 mm) Thick Moulded Samples under 1 kg and 5 kg Loads			
Blend	Flow Improving Additive	Vicat Softening Temperatures (° C)	
		1 kg Load	5 kg Load
1	None	82.6	75.1
2	8 phr B	82.0	74.0
3	8 phr C	83.5	74.3

Claims**1. A composition comprising:**

a) polymer of vinyl chloride;

b) core/shell polymer which acts to reduce the melt viscosity of (a) and comprises:

1) a core of polymer comprising at least 80 weight percent of units of (C₄ to C₁₂)- alkyl (meth)-acrylate and free from units derived from graftlinking or crosslinking monomer, the core polymer



Table 3

Notched Izod Impact Measurements for 1/8" (3.175 mm) Thick Samples							
Blend	Flow Improving Additive	Notched Izod Impact Strength (J/m)					
		15 °C		18 °C		23 °C	
		Hinge	Complete	Hinge	Complete	Hinge	Complete
1	None	--	70	--	161	1178	--
2	8 phr B	975 (60%)	179 (40%)	984	--	1092	--
3	8 phr C	--	197	904 (40%)	317 (60%)	947	--

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		18 °C		23 °C	
		Hinge	Complete	Hinge	Complete
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3	8 phr C	83.5	74.3

Claims

1. A composition comprising:

a) polymer of vinyl chloride;

b) core/shell polymer which acts to reduce the melt viscosity of (a) and comprises:

1) a core of polymer comprising at least 80 weight percent of units of (C₄ to C₁₂)- alkyl (meth)-acrylate and free from units derived from graftlinking or crosslinking monomer, the core polymer



being substantially non-crosslinked;

2) a subsequent shell stage of crosslinked polymer comprising:

A) at least 90 weight percent of units of vinyl aromatic monomer and/or (C₁ to C₄)-alkyl (meth)acrylate;

B) from 0.5 to 10 weight percent of units of:

(a) copolymerizable unsaturated acid of which from 10 to 100% by weight are in the form of an alkali, alkaline earth, or transition metal salt; and, optionally,

(b) multifunctional monomer containing two or more copolymerizable double bonds; and, optionally,

(3) a final shell stage of polymer containing at least 70 weight percent of units of vinyl aromatic monomer and/or (C₁ to C₄)-alkyl methacrylate.

2. A composition as claimed in Claim 1, wherein the polymer of vinyl chloride is homopolymer of vinyl chloride or copolymer containing at least 80 weight percent units of vinyl chloride and up to 20 weight percent of units derived from one or more of propylene, ethylene, vinyl acetate, vinylidene chloride, or (C₁ to C₄)-alkyl acrylate.

3. A composition as claimed in Claims 1 or 2, wherein the polymer of vinyl chloride has a weight-average molecular weight of from 40,000 to 120,000 or a Fikentscher K value of from 50 to 60.

4. A composition as claimed in any of Claims 1 to 3, containing from 2 to 15 parts of the additive polymer per 100 parts of the polymer of vinyl chloride.

5. A composition as claimed in any preceding Claim in the form of film, sheet, or other extruded or injection-moulded object.

6. A core/shell polymer, suitable for use as a melt viscosity reducer for the PVC in a composition of any preceding claim, comprising:

(1) a core of polymer comprising at least 80 weight percent of units of (C₄-C₁₂)-alkyl (meth)acrylate and free from units derived from graftlinking or crosslinking monomer, the core polymer being substantially non-crosslinked;

(2) a subsequent shell stage of crosslinked polymer comprising:

(A) at least 90 weight percent of units of vinyl aromatic monomer and/or (C₁ to C₄)-alkyl (meth)acrylate;

(B) from 0.5 to 10 weight percent of units of:

(a) copolymerizable unsaturated acid of which from 10 to 100% by weight are in the form of an alkali, alkaline earth, or transition metal salt; and, optionally,

(b) multifunctional monomer containing two or more copolymerizable double bonds; and, optionally,

(3) a final, shell-stage, of polymer containing at least 70 weight percent of units of vinyl aromatic monomer and/or (C₁-C₄)-alkyl methacrylate.

7. A polymer as claimed in Claim 6, wherein the (C₄ to C₁₂)-alkyl(meth)acrylate is n-butyl acrylate and the (C₁-C₄)-alkyl methacrylate is methyl methacrylate.

8. A polymer as claimed in Claim 6 or 7 wherein the unsaturated acid comprises one or more of the carboxylic acids: methacrylic acid, acrylic acid, itaconic acid, maleic acid, fumaric acid, alpha-methylen-delta-methyladipic acid, and acryloxypropionic acid.

9. A polymer as claimed in any preceding claim, wherein the alkali salt is sodium.

10. A polymer as claimed in any preceding claim, wherein the weight average molecular weight of the core polymer is from 5000 to 100,000.

Patentansprüche

1. Zusammensetzung, umfassend:

a) ein Polymer aus Vinylchlorid;



- b) ein Kern/Hülle-Polymer, welches die Schmelzviskosität von (a) verringert und umfaßt:
- 1) einen Kern aus einem Polymer, das mindestens 80 Gewichtsprozent Einheiten eines (C₄ bis C₁₂)-Alkyl(meth)acrylates umfaßt und frei ist von Einheiten, die von einem Monomer zum Pffropfvernetzen oder Quervernetzen stammen, welches Kernpolymer im wesentlichen nicht quervernetzt ist;
 - 2) eine nachfolgende Hülle-Stufe aus einem quervernetzten Polymer, umfassend:
 - A) mindestens 90 Gewichtsprozent Einheiten eines vinylaromatischen Monomers und/oder C₁ bis C₄)-Alkyl(meth)acrylates;
 - B) von 0,5 bis 10 Gewichtsprozent Einheiten von:
 - (a) einer copolymerisierbaren, ungesättigten Säure, von der von 10 bis 100 Gew.-% in der Form eines Alkali-, Erdalkali- oder Übergangsmetallsalzes vorliegen; und gegebenenfalls
 - (b) eines multifunktionellen Monomers, welches zwei oder mehrere copolymerisierbare Doppelbindungen enthält; und, gegebenenfalls
 - 3) eine Hülle-Endstufe aus einem Polymer, welches mindestens 70 Gewichtsprozent Einheiten eines vinylaromatischen Monomers und/oder (C₁ bis C₄)-Alkylmethacrylates umfaßt.
2. Zusammensetzung, wie in Anspruch 1 beansprucht, worin das Polymer aus Vinylchlorid ein Homopolymer aus Vinylchlorid oder ein Copolymer ist, welches mindestens 80 Gewichtsprozent Einheiten aus Vinylchlorid und bis zu 20 Gewichtsprozent Einheiten, abgeleitet von einem oder mehreren von Propylen, Ethylen, Vinylacetat, Vinylidenchlorid oder (C₁ bis C₄)-Acrylat, enthält.
3. Zusammensetzung, wie in Anspruch 1 oder 2 beansprucht, worin das Polymer aus Vinylchlorid ein Gewichtsmittel des Molekulargewichts von 40 000 bis 120 000 oder einen Fikent'schen Wert von 50 bis 60 besitzt.
4. Zusammensetzung, wie in einem der Ansprüche 1, bis 3 beansprucht, welche 2 bis 15 Teile des Additivpolymers pro 100 Teile des Polymers aus Vinylchlorid enthält.
5. Zusammensetzung, wie in einem vorhergehenden Anspruch beansprucht, in der Form eines Films, einer Folie oder eines anderen extrudierten oder spritzgegossenen Gegenstandes.
6. Kern/Hülle-Polymer, geeignet zur Verwendung als ein Mittel zur Verringerung der Schmelzviskosität für das PVC in einer Zusammensetzung eines vorhergehenden Anspruches, umfassend:
- 1) einen Kern aus einem Polymer, das mindestens 80 Gewichtsprozent Einheiten eines C₄ bis C₁₂)-Alkyl(meth)acrylates umfaßt und frei ist von Einheiten, die von einem Monomer zum Pffropfvernetzen oder Quervernetzen stammen, welches Kernpolymer im wesentlichen nicht quervernetzt ist;
 - 2) eine nachfolgende Hülle-Stufe aus einem quervernetzten Polymer, umfassend:
 - A) mindestens 90 Gewichtsprozent Einheiten eines vinylaromatischen Monomers und/oder C₁ bis C₄)-Alkyl(meth)acrylates;
 - B) von 0,5 bis 10 Gewichtsprozent Einheiten von:
 - (a) einer copolymerisierbaren, ungesättigten Säure, von der von 10 bis 100 Gew.-% in der Form eines Alkali-, Erdalkali- oder Übergangsmetallsalzes vorliegen; und gegebenenfalls
 - (b) eines multifunktionellen Monomers, welches zwei oder mehrere copolymerisierbare Doppelbindungen enthält; und, gegebenenfalls
 - 3) eine Hülle-Endstufe aus einem Polymer, welches mindestens 70 Gewichtsprozent Einheiten eines vinylaromatischen Monomers und/oder (C₁ bis C₄)-Alkylmethacrylates umfaßt.
7. Polymer, wie in Anspruch 6 beansprucht, worin das (C₄ bis C₁₂)-Alkyl(meth)acrylat n-Butylacrylat und das (C₁ bis C₄)-Alkylmethacrylat Methylmethacrylat ist.
8. Polymer, wie in Anspruch 6 oder 7 beansprucht, worin die ungesättigte Säure eine oder mehrere der Carbonsäuren umfaßt: Methacrylsäure, Acrylsäure, Itaconsäure, Maleinsäure, Fumarsäure, alphaMethylen-delta-methyladipinsäure und Acryloxypropionsäure.
9. Polymer, wie in irgendeinem vorhergehenden Anspruch beansprucht, worin das Alkalisalz Natrium ist.
10. Polymer, wie in irgendeinem vorhergehenden Anspruch beansprucht, worin das Gewichtsmittel des Molekulargewichts des Kernpolymers von 5 000 bis 100 000 ist.



Revendications

1. Composition comprenant :

a) un polymère de chlorure de vinyle ;

b) un polymère coeur/gaine, qui a pour rôle de réduire la viscosité de (a) à l'état fondu, et qui comprend :

1) un coeur constitué d'un polymère comprenant au moins 80 % en poids de motifs de (méth)-acrylate d'alkyle en C_4 à C_{12} et ne comprenant pas de motifs dérivés d'un monomère de greffage ou de réticulation, le polymère de coeur étant essentiellement non réticulé ;

2) puis un étage de gaine, en un polymère réticulé, comprenant :

A) au moins 90 % en poids de motifs d'un monomère vinylaromatique et/ou d'un (méth)-acrylate d'alkyle en C_1 à C_4 ;

B) de 0,5 à 10 % en poids de motifs

(a) d'un acide insaturé copolymérisable, dont 10 à 100 % en poids se présentent sous la forme d'un sel d'un métal alcalin, d'un métal alcalino-terreux ou d'un métal de transition ; et éventuellement

(b) d'un monomère multifonctionnel contenant au moins deux doubles liaisons copolymérisables ; et éventuellement

3) un dernier étage de gaine, en un polymère contenant au moins 70 % en poids de motifs d'un monomère vinylaromatique et/ou de méthacrylate d'alkyle en C_1 à C_4 .

2. Composition selon la revendication 1, dans laquelle le polymère de chlorure de vinyle est un homopolymère de chlorure de vinyle ou un copolymère contenant au moins 80 % en poids de motifs de chlorure de vinyle et jusqu'à 20 % en poids de motifs dérivant d'un ou plusieurs des composés propylène, éthylène, acétate de vinyle, chlorure de vinylidène ou acrylate d'alkyle en C_1 à C_4 .

3. Composition selon les revendications 1 ou 2, dans laquelle le polymère de chlorure de vinyle a une masse moléculaire moyenne en masse de 40 000 à 120 000 ou une valeur K de Fikentscher de 50 à 60.

4. Composition selon l'une quelconque des revendications 1 à 3, contenant de 2 à 15 parties du polymère par addition pour 100 parties du polymère de chlorure de vinyle.

5. Composition selon l'une quelconque des revendications précédentes, sous forme d'un film, d'une feuille ou d'un autre objet moulé par extrusion ou par injection.

6. Polymère coeur/gaine pouvant être utilisé comme réducteur de viscosité à l'état fondu du PVC dans une composition selon l'une quelconque des revendications précédentes, comprenant :

1) un coeur constitué d'un polymère comprenant au moins 80 % en poids de motifs de (méth)-acrylate d'alkyle en C_4 à C_{12} et ne comprenant pas de motifs dérivés d'un monomère de greffage ou de réticulation, le polymère de coeur étant essentiellement non réticulé ;

2) puis un étage de gaine, en un polymère réticulé, comprenant :

A) au moins 90 % en poids de motifs d'un monomère vinylaromatique et/ou d'un (méth)acrylate d'alkyle en C_1 à C_4 ;

B) de 0,5 à 10 % en poids de motifs

(a) d'un acide insaturé copolymérisable, dont 10 à 100 % en poids se présentent sous la forme d'un sel d'un métal alcalin, d'un métal alcalino-terreux ou d'un métal de transition ; et éventuellement

(b) d'un monomère multifonctionnel contenant au moins deux doubles liaisons copolymérisables ; et éventuellement

3) un dernier étage de gaine, en un polymère contenant au moins 70 % en poids de motifs d'un monomère vinylaromatique et/ou de méthacrylate d'alkyle en C_1 à C_4 .

7. Polymère selon la revendication 6, dans lequel le (méth)acrylate d'alkyle en C_4 à C_{12} est l'acrylate de n-butyle, et le méthacrylate d'alkyle en C_1 à C_4 est le méthacrylate de méthyle.

8. Polymère selon la revendication 6 ou 7, dans lequel l'acide insaturé comprend un ou plusieurs des acides carboxyliques suivants : acide méthacrylique, acide acrylique, acide itaconique, acide maléique,



acide fumarique, acide α -méthylène- δ -méthyladiplique, et acide acryloxypropionique.

9. Polymère selon l'une quelconque des revendications précédentes, dans lequel le sel d'un métal alcalin est le sel de sodium.
10. Polymère selon l'une quelconque des revendications précédentes, dans lequel la masse moléculaire moyenne en masse du polymère de cœur est de 5000 à 100 000.

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