

Description**Background of the invention**

5 The present invention relates to polymers which are inherently tacky and, as formed, are functional as pressure-sensitive adhesives. More particularly, the adhesives of the instant invention have excellent room- and low-temperature performance and provide an ecologically safe replacement for solvent adhesives and many acrylic- and rubber-based emulsion adhesives. The adhesives of the instant invention are prepared by emulsion polymerization.

10 Adhesives are provided as solvent polymers, bulk polymers and emulsion polymers. Some exist as pressure-sensitive adhesives, while others require tackification to achieve this end.

In respect of the instant invention, U.S. Patent No. 3,275,589 to Alexander, et al. pertains to an adhesive for adhering polyolefin and similar hydrophobic polymers to themselves and to other materials. The polymers disclosed are tacky, but not pressure-sensitive adhesives and are obtained by the polymerization
 15 of 100 parts by weight of a monomer mixture comprising 30 to 40 parts by weight vinyl acetate and, correspondingly, 60 to 70 parts by weight of (a) a monoalkyl ester of an alpha beta ethylenically unsaturated monocarboxylic acid such as 2-ethyl hexyl acrylate, or (b) a dialkyl ester of an alpha beta ethylenically unsaturated dicarboxylic acid such as 2-ethyl hexyl maleate, or (c) a mixture of the two. When three monomers are employed, the three illustrated include vinyl acetate, di-2-ethyl hexyl maleate and 2-ethyl hexyl acrylate.

20 U.S. Patents Nos. 4,507,429, 4,694,056, and 4,725,639 to Lenney, and assigned to Air Products, Inc., pertain to a pressure-sensitive adhesive composition, and the products and method of making them, comprising a polymer of an acrylic ester and/or vinyl ester, an olefinically unsaturated carboxylic comonomer, and a polyolefinically unsaturated copolymerizable monomer employed to enhance the adhesive strength of the polymer. The polymer is formed by an aqueous emulsion polymerization in the presence of a stabilizer system containing hydroxy propyl methylcellulose and an ethoxylated acetylenic glycol. Product glass transition temperature may be as high as -15°C, limiting utility at reduced temperature.

30 U.S. Patents Nos. 4,753,846, 4,826,938 and 4,829,139, all to Mudge and assigned to National Starch & Chemical Corporation, pertain to an ethylene containing pressure-sensitive adhesive produced by high-pressure emulsion polymerization in which the adhesive comprises a polymer of 30 to 70 percent by weight of a vinyl ester of an alkyl acid such as vinyl acetate, 10 to 30 percent by weight of ethylene, 20 to 40 percent by weight of di-2-ethyl hexyl maleate, and 1 to 10 percent by weight of a monocarboxylic acid such as acrylic acid. Again, glass transition temperature may be as high as -25°C, also limiting low-temperature utility.

U.S. Patent No. 4,322,576 assigned to Wacker Chemie GmbH also pertains to ethylene containing vinyl acrylate polymers also produced and formed by high-pressure emulsion polymerization. Dialkyl esters of dicarboxylic acids are not employed as monomers.

40 We have sought to develop pressure-sensitive adhesives of controlled properties which serve to supplant a multitude of solution and emulsion polymers by having broad utility and excellent adhesive properties at ambient and low temperatures. This is the subject of the instant invention.

US-A-4,564,664 discloses a tacky, pressure-sensitive adhesive polymer produced from certain monomers employed in the practice of the present invention. The prior process employs as one of the monomers a diester of an unsaturated dicarboxylic acid, specifically dibutyl fumarate thus having only 4 C atoms in each alkyl group, and importantly no vinyl-containing surfactant is employed. In contrast, in the present invention a vinyl-containing surfactant is used, which becomes an integral part of the polymer, and the diesters of unsaturated dicarboxylic acids used in this invention have ester groups each possessing 8 to 16 C atoms.

50 EP-A-0 220 885 discloses a pressure-sensitive adhesive which is a mixture of an emulsifiable adhesive, such as polyvinyl acetate modified acrylic adhesive, and a copolymer formed from the following monomers: a terminally unsaturated vinyl monomer and a vinyl unsaturated polymerizable emulsifier monomer.

Summary of the invention

55 According to the present invention, there is provided inherently tacky acrylic emulsion adhesive polymers having excellent adhesion to a wide variety of surfaces ranging from polar, relatively high energy surfaces such as stainless steel to nonpolar, relatively low energy surfaces such as polyethylene and to difficult-to-bond surfaces such as corrugated board. Moreover, cohesion and adhesion at low temperatures

is excellent and, when part of a laminate stock such as pressure-sensitive adhesive label stock, provides excellent high-speed converting characteristics such as die cutting, matrix stripping and fan folding. Superior properties are obtained even at lower-than-normal coat weights. In sum, the adhesive polymers are broad-based and serve to replace many solvent-based adhesives on an ecologically safe basis as well as many emulsion-based adhesives, thus serving a variety of markets.

According to the present invention, there is provided an inherently tacky, pressure-sensitive adhesive polymer formed by emulsion polymerization, which polymer comprises, on a polymerized basis and based on the total weight of the monomers forming the polymer:

(a) at least one alkyl acrylate containing from 4 to 8 carbon atoms in the alkyl group, the total amount of alkyl acrylate present being from 35 to 60 percent by weight;

(b) at least one vinyl ester containing from 2 to 16 carbon atoms in the alkyl group of the acid, the total amount of the vinyl ester present being from 15 to 35 percent by weight;

(c) at least one diester of an unsaturated dicarboxylic acid in which each alkyl group of the diester independently contains from 6 to 12 carbon atoms, the total of the diesters present being in an amount from 20 to 40 percent by weight; and

(d) at least one unsaturated carboxylic acid containing from 3 to 5 carbon atoms, the total of the unsaturated carboxylic acid being present in an amount up to 5 percent by weight, said polymer being formed in the presence of a vinyl-containing surfactant, said polymer having a glass transition temperature of less than about -30°C and a gel content of from 50 to 70 percent by weight of the polymer.

The emulsion adhesive polymers of the invention are prepared by using the said surfactant which polymerizes and becomes part of the emulsion polymer and which has been observed to enhance cohesive strength and aid in copolymerization of the monomers in forming the emulsion pressure-sensitive adhesive polymers. The said surfactant employed in the preparation of the emulsion pressure-sensitive adhesives of the present invention can be present in an amount up to 0.4 percent by weight of the total monomers, preferably from 0.1 to 0.25 percent by weight. The preferred surfactants are anionic surfactants, such as sodium vinyl sulfonate and sodium styrene sulfonate.

The emulsion adhesives of the instant invention may be prepared with excellent conversions at reaction temperatures ranging from 70 to 85°C in the presence of from 0.5 to 1 percent by weight, based on the weight of the monomers forming the polymer, of a persulfate or equivalent catalyst, with the monomer mix being fed over a period of 4 to 5 hours. Reaction pH is from 2.5 to 4.0. Conversion is high, approaching 100 percent at the reaction conditions set forth above.

A process for producing our pressure-sensitive adhesive polymer (as defined hereinbefore) comprises:

(i) at least one alkyl acrylate containing from 4 to 8 carbon atoms in the alkyl group and present in a total amount of 35 to 65 percent by weight of the monomers forming the polymer;

(ii) at least one vinyl ester containing from 2 to 16 carbon atoms in the alkyl chain of the acid, the total of the vinyl esters being present in an amount of 15 to 35 percent by weight of the monomers forming the polymer;

(iii) at least one diester of an unsaturated dicarboxylic acid present in a total amount of from 20 to 35 percent by weight of the monomers forming the polymer, each diester independently containing from 8 to 16 carbon atoms in the alkyl group of the ester; and

(iv) up to 5 percent by weight of the monomers forming the polymer of at least one unsaturated carboxylic acid;

(v) from 0 to 10 percent by weight of the monomers forming the polymer of at least one chelating monomer;

to emulsion polymerization in the presence of a vinyl-containing surfactant by initiating polymerization of an initial monomer mix consisting of up to 10 percent of the total monomers in the presence of an initiator, and adding the balance of the monomers and the initiator therefor to the emulsion reaction system over a period of 4 to 5 hours to achieve a total solids content up to 60 percent by weight of the emulsion, said emulsion reaction being maintained under autogenous conditions at a temperature of 70 to 85°C and a pH of from 2 to 4 in the presence of a stabilizer system comprising an anionic and a nonionic surfactant system, in which the anionic-to-nonionic surfactant ratio is 3 to 1, said polymer having a gel content of 50 to 70 percent by weight.

The polymers may be modified using cross-linking reactions induced by metal salts, organometallic complexes, electron beam radiation, actinic radiation, or heat. A significant improvement in cohesive strength can be achieved without much loss of peel and tack by incorporating small amounts of chelating monomers having at least one active methylene group in the pendent chain, with or without a chain transfer agent, and additionally by crosslinking the polymers using metal salts such as aluminum acetate.

Detailed Description

The present invention relates to pressure-sensitive adhesive compositions based on emulsion polymers which provide high adhesion and high tack to polar, nonpolar and difficult-to-bond substrates with excellent cohesion. The adhesives have properties sufficient to make them useful for replacing solvent polymers, tackified styrene-butadiene emulsion pressure-sensitive adhesives, and nontackified and tackified acrylic pressure-sensitive adhesives. An improvement exhibited over tackified styrene-butadiene resin adhesives include better aging and no edge ooze or bleed as part of a release liner adhesive face stock laminate. In addition, being functional as a single polymer, there is a minimal or no need for compounding and tackification. The improved performance characteristics of the adhesive of the instant invention enable them to be used on almost any available face stock. Properties induced in the adhesive by proper selection of monomers and surfactants give excellent moisture resistance enabling the adhesive to be used for medical and moisture-resistant pressure-sensitive adhesive applications.

As compared to prior art acrylic pressure-sensitive adhesives which do not give good adhesion to nonpolar surfaces, such as polyolefins and certain other surfaces such as recycled corrugated board, without tackification with attendant sacrifice in cohesive strength and low-temperature performance, the adhesives prepared in accordance with the instant invention have excellent adhesion to both polyolefins and corrugated board and good low-temperature performance. The adhesives are more universal in their use, a result not heretofore achieved in single polymer adhesives.

The emulsion based pressure-sensitive adhesives of the instant invention contain, on a percent by weight basis from 35 to 60 percent by weight total, one or more alkyl acrylates containing 4 to 8 carbon atoms in the alkyl groups, and preferably total alkyl acrylate concentration, including mixtures of alkyl acrylates, preferably present in a total amount of from 40 to 50 percent by weight of the monomers. Useful alkyl acrylates include n-butyl acrylate, 2-ethyl hexyl acrylate, and isooctyl acrylate, with 2-ethyl hexyl acrylate being preferred.

The second monomeric component is one or more vinyl esters present in a total amount of from 15 to 35 percent by weight, preferably from 20 to 25 percent by weight based on total weight of the monomers, said vinyl esters containing from 2 to 16 carbon atoms in the alkyl group of the acid. Representative of the vinyl esters include vinyl acetate, vinyl butyrate, vinyl propionate, vinyl isobutyrate, vinyl valerate, and vinyl versatate. Vinyl acetate is preferred.

The third component of the emulsion polymers of the instant invention are one or more diesters of an unsaturated dicarboxylic acid and mixtures thereof, present in a total amount of from 20 to 35 percent by weight based on the total weight of the monomers. Each ester group of the diester independently contains from 8 to 16, preferably from 8 to 12, carbon atoms. The preferred diesters are di-2-ethyl hexyl maleate, di-2-ethyl hexyl fumarate and mixtures thereof.

A fourth component of the instant invention is at least one unsaturated carboxylic acid containing from 3 to 5 carbon atoms and present in a total amount of up to 5 percent by weight of the polymer, preferably from 1 to 3 percent by weight. The unsaturated carboxylic acid includes, among others, acrylic acid, methacrylic acid and itaconic acid. Acrylic acid, methacrylic acid, and more preferably mixtures thereof, are presently preferred.

The emulsion adhesives of the instant invention are prepared in the presence of a vinyl-containing surfactant which polymerizes during formation of the polymer and becomes an integral part of the polymer. Preferred reactive surfactants include vinyl-containing monomers such as sodium vinyl sulfonate and sodium styrene sulfonate. The reactive surfactant is present as part of the total surfactant system and in an amount up to 0.4 percent by weight of the total monomers, preferably 0.1 to 0.25 percent by weight.

Presently preferred emulsion polymers contain, exclusive of reactive monomers, 48 percent by weight 2-ethyl hexyl acrylate, 21 percent by weight vinyl acetate, 29 percent by weight di-2-ethyl hexyl maleate, 1 percent by weight acrylic acid, and 1 percent by weight methacrylic acid.

The monomer proportions are adjusted in such a way that the adhesive has a glass transition temperature less than about -30°C , preferably less than -34°C , giving a good balance of adhesion and tack at room temperature and low temperatures. The emulsion polymers of this invention have a very broad glass transition temperature range of from 15 to 30°C , e.g. -22 to -52°C , which is unusual among acrylic polymers. Conventional acrylic polymers, for instance, have a glass transition temperature range of only 10 to 15°C . Depending on polymerization conditions, copolymers showing two distinct glass transition temperatures, one in the region of -45 to -60°C and the other in the region of -15 to -30°C , have been observed.

Gel content or percent insolubles are in the range of 50 to 65 percent by weight which provides excellent cohesive strength without the use of multifunctional monomers. In this regard, gel represents the

amount of polymer which is insoluble in tetrahydrofuran expressed in percent by weight and determined by the membrane gel partitioning method. In this method, about 600 to 800 milligrams of 100 percent solid polymer is weighed onto a Millipore® membrane disk of 5 µm porosity. The disk is heat sealed and transferred to a scintillation vial. About 20 milliliters of tetrahydrofuran is added to the vial and the vial is rotated on a shaker for 16 to 24 hours. The sealed disk is then removed, washed with tetrahydrofuran, and dried first by placing it on a whatman No. 1 filter paper, followed by exposure to 100°C in the oven for a few hours. The dried disk is weighed and the insoluble portion of the polymer determined by the equation:

$$\text{Per cent insoluble} = \frac{(b - c) \times 100}{a} = \% \text{ gel}$$

wherein

- a = total weight of 100 percent solids polymer
- b = the weight of the polymer plus membrane before tetrahydrofuran treatment
- c = polymer plus membrane remaining after tetrahydrofuran treatment.

Polymer properties can be further modified to fit end use applications by inclusion of multifunctional monomers and the use of other chemical cross-linking agents. Other aids which may be used to develop cross-linking include thermal cross-linking and cross-linking by actinic and electron beam radiation.

Polymers of the instant invention are prepared by emulsion polymerization under conditions of agitation in an autogenous atmosphere in the presence of suitable polymerization initiators such as peroxydisulfate and peroxides. Depending on desired polymer properties including gel content, the preferred levels of these initiators are in the range of from 0.5 to 1.0 percent by weight based on the total weight of the monomers. The presently preferred initiators are potassium persulfate, and t-butyl hydrogen peroxide. Level of agitation will vary depending on the system and will influence conversion. Typically, 30 to 50 percent of the total initiator is added along with an initial monomer charge to the reactor, and the rest is added along with the balance monomers during polymerization over a period of from 4 to 5 hours. For the polymer to be free from coagulum and to maintain grit levels less than 20 ppm, it is desirable to maintain the pH of the emulsion during polymerization between from 2 to 4, preferably from 2.5 to 4. This can be achieved by the use of buffers such as sodium bicarbonate and sodium acetate, typically in amounts up to 0.3 percent by weight based on the weight of the monomer.

The stabilizer system used during polymerization contains a combination of anionic and nonionic surfactants present in an amount up to about 3.5 percent by weight based on the weight of the monomers. A suitable anionic surfactant is the sodium salt of an ethoxylated nonylphenol sulfate, and a suitable nonionic surfactant is ethoxylated nonylphenol. The best balance of properties is achieved by maintaining the anionic to nonionic surfactant ratio approximately 3 to 1.

Polymers of the instant invention are produced at high solids level content, typically 50 to 70 percent by weight. Reaction is carried out at temperatures from 70 to 85°C with an initial charge of up to 10 percent by weight of the total monomers, with the balance of the monomers being added to the emulsion reaction system over a period of 4 to 5 hours, with total monomer conversion approaching 100 percent.

It is possible to modify the rheology of the polymer for coating purposes by use of conventional thickeners such as SCT-270® manufactured and sold by Union Carbide and present in an amount up to 0.2 percent by weight. Although not required, it is also feasible to modify the properties by the use of tackifiers and the like. For general purpose applications, it is desirable to have good adhesion to both hydrophobic substrates such as polyethylene and hydrophilic substrates such as stainless steel and difficult-to-bond recycled corrugated board. Prior art acrylic polymers do not have good adhesion to such substrates unless they are modified by addition of a tackifier. This is not required using the pressure-sensitive adhesive polymer of this invention although tackifiers can be effectively used to tailor adhesion to a substrate.

It is also feasible, in accordance with the present invention, to provide emulsion pressure-sensitive adhesive polymers with high shear performance even at elevated temperature with little or no detriment in peel and tack adhesion which can be used to replace high cost solvent acrylic polymers used in film applications. Such polymers can be tackified to enhance adhesion to low energy substrates such as polyolefins even at low temperatures. The dioctyl maleate in the composition provides tackiness to the adhesive and allows the use of vinyl acetate which provides good peel adhesion without the use of high levels of acid monomer which tends to reduce tack.

Improved shear may be achieved by copolymerization with small amounts, i.e., 0.1 to 1 percent by weight of the monomers, of functional chelating monomers such as acetoacetoxy ethyl methacrylate

(AAEMA), which have a pendent chain with at least one active methylene group, and which enable complex formation with metal salts. As used herein, the term "active methylene group" refers to a functional group capable of exhibiting keto-enol tautomerism and anion formation.

The presence of the chelating monomer in the copolymer itself provides some improvement in shear performance which may not be sufficient enough for high performance film applications. Further cross-linking by complex formation with metal salts dramatically enhances the shear in excess of 10,000 min. Elevated temperature (70°C) shear is also greatly improved, equalling the performance of the emulsion polymers to solvent acrylic systems. Adding chelating monomers to the copolymer may alter the gel content and/or glass transition temperature of the adhesive. Accordingly, when chelating monomers are used, they are added in an amount that yields an adhesive that is pressure-sensitive, i.e., the glass transition temperature is sufficiently low as to enable use as a PSA. The mechanism of using chelating monomers is described, for instance, in U.S. Patent 4,354,008 to Skoltchi, and U.S. Patent 4,908,403 to Spada, et al.

To maintain good balance of peel and tack with high shear it is desirable to lower the molecular weight of the polymer by the use of chain transfer agents such as n-dodecyl mercaptan (n-DDM) and to use higher levels of initiator than what is commonly used. An optimum level of n-DDM in this invention is up to 0.025 percent by weight of the monomers, preferably 0.005 to 0.01 percent by weight, and to employ a level of initiator of 0.6 to 0.75 percent by weight based on the weight of the monomer composition. Amounts exceeding these levels can result in cohesive failure in peel adhesion on certain substrates which will be detrimental to the product application. Polymers with low levels of initiator provide high shear with AAEMA and aluminum acetate (AA) cross-linking, but only with loss of peel and tack adhesion. Aluminum acetate, if present, is normally present in an amount up to 0.25 percent by weight of the monomers. However, the polymer containing the chain transfer agent and a higher level of initiator gives high shear with little or no loss in adhesion properties.

The high shear associated with the modified polymer makes it suitable for tackification with conventional tackifiers such as Snowtack® line resins sold by Albright Wilson Co. and Aquatac® resins sold by Arizona Chemicals expressly to enhance adhesion to low energy substrates such as polyolefins. For such applications, it is generally necessary to provide a glass transition temperature, e.g., below -30°C. The T_g of the polymer can be as low as -40°C to promote good adhesion to low energy substrates at low temperatures as low as -5°C without sacrificing the room-temperature properties. This is done by increasing the ratio of the soft monomer to vinyl acetate in the total composition.

Examples 1 to 4 and Controls 1 and 2

To a one liter reactor equipped with a reflux condenser, a thermocouple, a pitched turbine agitator and a nitrogen inlet tube, there was charged a solution containing 75 g of deionized water, 4 g of sodium vinyl sulfonate (25 percent w/w solution in water) and 0.36 g of an anionic surfactant (Alipal CO-433®, a sodium salt of ethoxylated nonylphenol sulfate manufactured and sold by GAF Chemical Co.). A monomer mix consisting of 215 g of 2-ethyl hexyl acrylate, 150 g of di-2-ethyl hexyl maleate, 125 g of vinyl acetate, 5 g of acrylic acid and 5 g of methacrylic acid was added to 115 g of water containing 44.63 g of Alipal CO-433® and 6.44 g of Igepal CO-887®, an ethoxylated nonylphenol nonionic surfactant manufactured and sold by GAF Chemical Co., and agitated to make a pre-emulsion. The reactor charge was heated under nitrogen to 70°C, to which was added 24.25 g of a potassium persulfate solution (3.78 percent w/w solution in deionized water). Sixty-six grams of the pre-emulsified monomer and 12.125 g of potassium persulfate solution were added to the reactor over 20 to 30 minutes. After the temperature reached a steady state, the remaining monomer pre-emulsion and a 1.8 percent aqueous solution of potassium persulfate buffered with sodium bicarbonate were introduced into the reactor at respective rates of 2.5 and 0.32 g/min. for a period of about 240 minutes. The reactor temperature was maintained between 79 to 82°C. After the end of feed, the reactor temperature was raised to 83 to 85°C and maintained for 90 minutes. Once the polymerization was complete, the contents were cooled to ambient temperature and discharged. The polymer had 59.27 percent solids, 0.01 percent coagulum, Brookfield viscosity (spindle number 3 at 12 rpm) of 2500 cps, a final pH of 3.8, and a T_g of -28.5°C.

Using the above procedure the polymers listed in Table 1 were also prepared.

Table 1

	Monomer Composition	Weight Ratio	Percent Solids	pH
EX.2	2-EHA ¹ /DOM ² /VAc ³ /AA ⁴	43/30/25/2	59.7	4.35
Ex.3	2-EHA/DOM/VAc/AA/MAA ⁵	48/29/21/1/1	59.6	3.80
Ex.4	2-EHA/DOM/VAc/AA/MAA	50/27/21/1/1	59.3	3.54

¹ 2-ethyl hexyl acrylate² dioctyl maleate³ vinyl acetate⁴ acrylic acid⁵ methacrylic acid

Similar polymers were made using the same procedure, but replacing Alipal CO-433® with Polystep B-27®, manufactured and sold by Stepan Chemicals, and replacing Igepal CO-887® with Polystep F-9®, also manufactured and sold by Stepan Chemicals.

Table 2 compares the adhesive performance of the adhesive of Example 3 to commercial pressure-sensitive adhesive (Controls 1 and 2) at room temperature. Better overall properties and superior room-temperature shear were achieved.

Table 2

	Ct.Wt. g/sqm	90° Peel N/m ⁸			Loop Tack N/m ⁹			RIS ¹⁰ Min.
		SS ¹¹	PE ¹²	CB ¹³	SS	PE	CB	
Ex. 3	22-25	480	330	280	740	520	360	140c
Control 1 ⁶	23-26	310	350	150	650	525	300	30c
Control 2 ⁷	23-26	710c	230	315c	720	460	400	5c

⁶ Tackified SBR adhesive⁷ Cargill 6441®, a commercial polymer sold by Cargill Inc. and containing the same monomers used in this invention

c = cohesive failure

⁸ PSTC No. 2, 5th Ed.⁹ PSTC No. 5, 6th Ed.¹⁰ Room-temperature shear = PSTC No.7, 6th Ed. (500g load)¹¹ Stainless steel¹² Treated high density Polyethylene¹³ Recycled corrugated board

Tackified SBR (Control 1) shows a lower adhesion to corrugated board and has a low cohesive strength. Besides this, Control 1 had a tendency to exhibit bleed and edge ooze on aging, which make the adhesive nonuseful with certain face stocks. The Cargill 6441® (Control 2) lacked cohesive strength and displayed a cohesive mode of failure for peel adhesion, which make it of questionable acceptability for label applications.

Example 5 and Comparative Example 6

Experiments were performed with and without the vinyl-containing surfactants, i.e. sodium vinyl sulfonate (SVS), to establish its effects on shear performance.

As can be seen from Table 3, Example 5 gives room-temperature shear values comparable to Example 3, whereas Comparative Example 6, containing no SVS, gives lower shear values.

Table 3

Sample	Percent Solids	90° Peel N/m	L. Tack N/m	RTS ^a Min.
		SS	SS	SS
Ex. 5	59.8	370	670	130c
Comparative Ex.6	59.8	355	700	58c

^a 500 g load

There is an apparent improvement in shear for the polymer with the use of SVS. SVS has been observed to also control the viscosity of the emulsion polymer to accommodate high solids and for good conversion. With no SVS, the viscosity is less consistent and is higher than the polymer prepared using SVS (5000 to 15000 cps vs. 3000 to 5000 cps).

Control 3

Further experiments with the composition of the present invention have been carried out to obtain gel content similar to that of the Cargill 6441 polymer for a better comparison.

To obtain Control 3, therefore, Example 3 was repeated with the difference that the preemulsion contained 0.125 g of n-dodecyl mercaptan, a chain transfer agent, the total initiator was 5 g and the total feed time was 270 minutes. Table 4 provides the comparative properties of Examples 1 and 3 to each other and to the Cargill 6441® polymer and the polymer of Control 3. Examples 1 and 3 give very good room-temperature performance with good shear. The polymer of Control 3, with a lower gel content similar to Cargill 6441®, had a very low shear performance combined with cohesive mode of failure for peel adhesion.

Table 4 shows the low-temperature performance obtained for the pressure-sensitive adhesives of the present invention compared to Example 1 and Control 3 and the Cargill 6441®. Example 3 shows good adhesion and good fiber pick on recycled corrugated board, and good adhesion and face stock tear on treated high density polyethylene. Example 1, with higher Tg, had better room-temperature performance than low-temperature performance. Control 3 and Cargill 6441®, with low cohesion, showed only fair adhesion.

Table 4

Low-Temperature Performance Properties					
Period	Ct.Wt. g/sqm	% Gel	Tg, °C	25° Peel Adhesion ¹³	
				RCB	TRHDPE
Ex. 1	26	53	-28	F-P/CL	F/CL
Ex. 3	23	58	-34	G/GFP	G/SIFT
Control 3	23	25	-36	F/SIFT	F/CL
Cargill 6441®	23	20	-27	F/VsIFP	F/CL

¹³ practical peel adhesion determined by subjective hand testing

RCB = recycled corrugated board

TRHDPE = treated high density polyethylene

G = good adhesion

F = fair adhesion

P = poor adhesion

CL = removes clean

GFP = good fiber pick

VsIFP = very slight fiber pick

SIFT = slight face tear

Examples 6 to 10 and Controls (Ctl) 4 to 6

To a one liter reactor equipped with a reflux condenser, a thermocouple, a pitched turbine agitator and a nitrogen inlet tube, there was charged a solution containing 75 g of deionized water, 2 g of sodium vinyl sulfonate (25 percent solution in water) and 0.36 g of Polystep F-27® emulsifier. A monomer mix consisting of 237.5 g of 2-ethyl hexyl acrylate (2-EHA), 145 g of dioctyl maleate (DOM), 105 g of vinyl acetate (VA), 7.5 g of acrylic acid (AA), 2.5 g of methacrylic acid (MAA), 2.5 g of acetoacetoxy ethyl methacrylate (AAEMA), and 0.25 g of n-dodecyl mercaptan (n-DDM) was added to 115 g of water containing 44.63 g of Polystep B-27® and 6.44 g of Polystep F-9® and agitated to make a pre-emulsion. The reactor charge was heated to 72 to 75 °C and there was added 24.25 g of 4.37 percent w/w of potassium persulfate solution. Sixty-six grams of the pre-emulsified monomer and 12.13 g of the potassium persulfate solution were added over 20 to 30 minutes. After the temperature reached a steady state, the remaining monomer pre-emulsion and a 2.21 percent aqueous solution of potassium persulfate buffered with sodium bicarbonate were introduced into the reactor at respective rates of 2.22 and 0.29 g/min. over a period of 270 minutes. The reaction temperature was maintained between 79 to 82 °C. After the end of feed, process temperature was raised to 83 to 85 °C. Thirty minutes after the feed, 5.25 g of a 4.8 percent solution of potassium persulfate was added and the reactants maintained for 90 minutes. Once the polymerization was complete, the contents were cooled to ambient temperature, neutralized with ammonia to pH 5.5 to 6.5, and discharged. The polymer content was 60 percent solids, with less than 0.02 percent coagulum. Polymer Tg was -35 °C.

Using the same procedure, the polymers listed in Table 5 were prepared, except for examples 9 and 10 where the initial charge had 3.85 percent solution of initiator and the main feed had 1.9 percent solution of initiator.

Table 5

Percent Example	Monomer Composition	Wt. Ratio	Solids
Ex. 7	2-EHA/DOM/Vac/n-DDm/AA/MAA	48/29/21/0.005/1.5/0.5	59.0
Ex. 8	2-EHA/COM/VAc/AAEMA/AA/MAA/n-DDm/BA	47.5/25/17/0.5/1.5/0.5/0.005/8	59.5
Ex. 9	2-EHA/DOM/VAc/BA/AA/MAA/n-DDM	48/24/16/10/1.5/0.5/0.005	58.9
Ex. 10	2-EHA/DOM/VAc/AA/MAA/AAEMA	48/29/20.5/1/1/0.5	59.3

Table 6 shows the adhesive properties of Examples 6 to 10 against, for purposes of these Examples, controls which are polymers made by the procedure of Example 11 with similar composition but not containing n-DDM or AAEMA. As in all other examples, shear was measured using a sample measuring 1,27 cm x 1,27 cm (1/2" x 1/2"). Shear values (both RTS and 70 °C shear) were determined using a 500 g load, and measured in minutes. The polymers of Examples 6 to 10 show better overall properties. Example 2 and 9, with no AAEMA and with only ionic cross-linking with aluminum acetate (AA), gave shear values much less than Example 6. Example 10, containing no n-DDM and polymerized with a lesser level of initiator, had a good shear value, although the adhesion properties were lower. In the Controls, the improvement of shear is not dramatic, and just cross-linking with aluminum acetate reduces adhesion values. A combination of chain transfer agent (n-DDM) and the higher level of initiator give low molecular weight polymers which provide good adhesion values and high shear.

Table 6

	Ct.Wt. g/sqm	AA Wt. %	AAEMA Wt. %	90° Peel N/m	Loop Tack N/m	RTS, Min.	70° C Shear Min.
Ex. 6	23	0.06	0.5	295	510	10000 +	4000 +
Ex. 7	23	0.15	---	295	480	1600	---
Ex. 8	23	0.15	0.5	245	310	10000 +	---
Ex. 9	23	0.15	---	250	353	2300	---
Ex. 10	28	0.06	0.5	240	400	7000 +	---
Ctl. 4	21	0.06	---	250	320	600	---
Ctl. 5	23	0.20	---	250	340	2200	---
Ctl. 6	27	---	---	330	540	210	---
Release liner = 1100							
Face stock = 2 mil Mylar®							

Examples 11 to 18

Using the general procedure described above, additional emulsion polymers were made by varying the amount of monomers and acetoacetoxy ethyl methacrylate, as shown in weight percent in Table 7. The initiator level was maintained between 0.6 and 0.7% based on the total monomer weight, and the n-dodecyl mercaptan level was maintained below 0.015% by weight.

Table 7

Ex.	2-EHA	VAC	DOM	AA	MAA	AAEMA	Other Monomers
11	47.75	21	29	1.5	0.5	0.25	---
12	47.9	21	29	1.5	0.5	0.1	---
13	48	21	28	2	1	0.15	---
14	43	25	29	2	1	0.15	---
15	48	20	28	1.5	1.5	0.1	1.0 t-octyl acrylamide
16	43	25	27.55	1.5	0.5	0.15	0.3 amide, 2 HPA
17	43	25	29.65	1.5	0.5	0.15	0.2 MAEEU
18	52.4	20	24.85	2	0.75	0.15	---
Amide = Acrylamide							
HPA = Hydroxypropyl acrylate							
MAEEU = Methacrylamide of aminoethyl ethylene urea							

The emulsion polymers were coated and dried, and tested using polyester facestock in pressure-sensitive adhesive construction. Table 8 gives the initial and one week at 70° C aged performance data on a stainless steel test panel. All of the polymers show good adhesion with high cohesion. Even the polymers containing low levels of acetoacetoxy ethyl methacrylate (e.g., example 12 show shear values in excess of 6000 minutes. The plus sign after the shear values indicate that the samples were removed after that time and that the test was discontinued.

Table 8

Ex.	Ct.Wt. g/sqm	180° Peel N/m		Loop Tack N/m		RTS 500 g Min.
		20 Min	1/Wk, @70° C	Init.	1/Wk, @70° C	
11	25	450	350	485	330	10000 +
12	27	570	---	485	---	6000 +
13	30	450	350	600	360	6000 +
14	25	470	380	600	370	5000 +
15	25	520	445	500	500	2000- 4000
16	25	420	355	390	235	---
17	24	455	480	480	440	10000 +
18	24	350	---	425	---	10000 +

Claims

1. An inherently tacky, pressure-sensitive adhesive polymer formed by emulsion polymerization, which polymer comprises, on a polymerized basis and based on the total weight of the monomers forming the polymer:
 - (a) at least one alkyl acrylate containing from 4 to 8 carbon atoms in the alkyl group, the total amount of alkyl acrylate present being from 35 to 60 percent by weight;
 - (b) at least one vinyl ester containing from 2 to 16 carbon atoms in the alkyl group of the acid, the total amount of the vinyl ester present being from 15 to 35 percent by weight;
 - (c) at least one diester of an unsaturated dicarboxylic acid in which each alkyl group of the diester independently contains from 6 to 12 carbon atoms, the total of the diesters present being in an amount from 20 to 40 percent by weight; and
 - (d) at least one unsaturated carboxylic acid containing from 3 to 5 carbon atoms, the total of the unsaturated carboxylic acid being present in an amount up to 5 percent by weight, said polymer being formed in the presence of a vinyl-containing surfactant, said polymer having a glass transition temperature of less than about -30° C and a gel content of from 50 to 70 percent by weight of the polymer.
2. A pressure-sensitive adhesive polymer as claimed in claim 1 in which the alkyl acrylate is present in a total amount of from 40 to 50 percent by weight of the monomers forming the polymer.
3. A pressure-sensitive adhesive polymer as claimed in any one of claims 1 or 2 in which the vinyl ester is present in a total amount of from 20 to 25 percent by weight based on the total weight of the monomers forming the polymer.
4. A pressure-sensitive adhesive polymer as claimed in any one of claims 1 to 3 in which the vinyl ester is vinyl acetate.
5. A pressure-sensitive adhesive polymer as claimed in any one of the previous claims in which the diester of the unsaturated dicarboxylic acid independently contains from 8 to 12 carbon atoms in each alkyl group.
6. A pressure-sensitive adhesive polymer as claimed in any one of the previous claims in which the diester of the unsaturated dicarboxylic acid is selected from the group consisting of di-2-ethyl hexyl maleate, di-2-ethyl hexyl fumarate, and mixtures thereof.
7. A pressure-sensitive adhesive polymer as claimed in any one of the previous claims in which the unsaturated carboxylic acid is present in an amount of from 1 to 3 percent by weight of the total monomers forming the polymer.



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Claims

1. An inherently tacky, pressure-sensitive adhesive polymer formed by emulsion polymerization, which polymer comprises, on a polymerized basis and based on the total weight of the monomers forming the polymer:
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 - (b) at least one vinyl ester containing from 2 to 16 carbon atoms in the alkyl group of the acid, the total amount of the vinyl ester present being from 15 to 35 percent by weight;
 - (c) at least one diester of an unsaturated dicarboxylic acid in which each alkyl group of the diester independently contains from 6 to 12 carbon atoms, the total of the diesters present being in an amount from 20 to 40 percent by weight; and
 - (d) at least one unsaturated carboxylic acid containing from 3 to 5 carbon atoms, the total of the unsaturated carboxylic acid being present in an amount up to 5 percent by weight, said polymer being formed in the presence of a vinyl-containing surfactant, said polymer having a glass transition temperature of less than about -30°C and a gel content of from 50 to 70 percent by weight of the polymer.
2. A pressure-sensitive adhesive polymer as claimed in claim 1 in which the alkyl acrylate is present in a total amount of from 40 to 50 percent by weight of the monomers forming the polymer.
3. A pressure-sensitive adhesive polymer as claimed in any one of claims 1 or 2 in which the vinyl ester is present in a total amount of from 20 to 25 percent by weight based on the total weight of the monomers forming the polymer.
4. A pressure-sensitive adhesive polymer as claimed in any one of claims 1 to 3 in which the vinyl ester is vinyl acetate.
5. A pressure-sensitive adhesive polymer as claimed in any one of the previous claims in which the diester of the unsaturated dicarboxylic acid independently contains from 8 to 12 carbon atoms in each alkyl group.
6. A pressure-sensitive adhesive polymer as claimed in any one of the previous claims in which the diester of the unsaturated dicarboxylic acid is selected from the group consisting of di-2-ethyl hexyl maleate, di-2-ethyl hexyl fumarate, and mixtures thereof.
7. A pressure-sensitive adhesive polymer as claimed in any one of the previous claims in which the unsaturated carboxylic acid is present in an amount of from 1 to 3 percent by weight of the total monomers forming the polymer.



8. A pressure-sensitive adhesive polymer as claimed in any of the previous claims in which the unsaturated carboxylic acid is acrylic acid, methacrylic acid, or mixtures thereof.
9. An inherently tacky emulsion pressure-sensitive adhesive polymer as claimed in claim 1 and comprising, on a polymerized basis, 48 percent by weight 2-ethyl hexyl acrylate, 21 percent by weight vinyl acetate, 29 percent by weight di-2-ethyl hexyl maleate, 1 percent by weight acrylic acid, and 1 percent methacrylic acid.
10. A pressure-sensitive adhesive polymer as claimed in any one of the previous claims in which a chelating monomer having at least one active methylene group present in the polymer.
11. A pressure-sensitive adhesive polymer as claimed in claim 10 in which the chelating monomer is present in an amount of up to 1 percent by weight of the monomers forming the polymer.
12. A pressure-sensitive adhesive polymer as claimed in claim 10 or 11 in which the chelating monomer is acetoacetoxy ethyl methacrylate.
13. A pressure-sensitive adhesive polymer as claimed in any one of the previous claims in which the reactive surfactant is sodium vinyl sulfonate, sodium styrene sulfonate, or mixtures thereof and the reactive surfactant is present in an amount up to 0.4 percent by weight based on the total weight of the monomers forming the polymer.
14. A pressure-sensitive adhesive polymer as claimed in any of the previous claims in which the reactive surfactant is present in an amount of 0.1 to 0.25 percent by weight of the total monomers forming the polymer.
15. A pressure-sensitive adhesive polymer as claimed in any one of the previous claims in which the polymer is formed in the presence of a chain transfer agent.
16. A process for the production of inherently tacky, pressure-sensitive adhesive emulsion polymers as claimed in any of claims 1 to 15 which comprises:
 - subjecting an emulsified mix of monomers comprising:
 - (i) at least one alkyl acrylate containing from 4 to 8 carbon atoms in the alkyl group and present in a total amount of 35 to 65 percent by weight of the monomers forming the polymer;
 - (ii) at least one vinyl ester containing from 2 to 16 carbon atoms in the alkyl chain of the acid, the total of the vinyl esters being present in an amount of 15 to 35 percent by weight of the monomers forming the polymer;
 - (iii) at least one diester of an unsaturated dicarboxylic acid present in a total amount of from 20 to 35 percent by weight of the monomers forming the polymer, each diester independently containing from 8 to 16 carbon atoms in the alkyl group of the ester; and
 - (iv) up to 5 percent by weight of the monomers forming the polymer of at least one unsaturated carboxylic acid;
 - (v) from 0 to 10 percent by weight of the monomers forming the polymer of at least one chelating monomer;
 - to emulsion polymerization in the presence of a vinyl-containing surfactant by initiating polymerization of an initial monomer mix consisting of up to 10 percent of the total monomers in the presence of an initiator, and adding the balance of the monomers and the initiator therefor to the emulsion reaction system over a period of 4 to 5 hours to achieve a total solids content up to 60 percent by weight of the emulsion, said emulsion reaction being maintained under autogenous conditions at a temperature of 70 to 85°C and a pH of from 2 to 4 in the presence of a stabilizer system comprising an anionic and a nonionic surfactant system, in which the anionic-to-nonionic surfactant ratio is 3 to 1, said polymer having a gel content of 50 to 70 percent by weight.

Patentansprüche

1. Inhärent klebendes, druckempfindliches Klebstoffpolymer, welches durch Emulsionspolymerisation gebildet wird und welches Polymer auf polymerisierter Basis und bezogen auf das Gesamtgewicht der das Polymer bildenden Monomeren umfaßt:



(a) wenigstens ein Alkylacrylat, welches 4 - 8 Kohlenstoffatome in der Alkylgruppe aufweist, wobei die Gesamtmenge des vorhandenen Alkylacrylats 35 - 60 Gew.-% beträgt;

(b) wenigstens einen Vinylester, der 2 - 16 Kohlenstoffatome in der Alkylgruppe der Säure aufweist, wobei die Gesamtmenge des vorhandenen Vinylesters 15 - 35 Gew.-% beträgt;

(c) wenigstens einen Diester einer ungesättigten Dicarbonsäure, in welchem jede Alkylgruppe des Diesters unabhängig voneinander 6 - 12 Kohlenstoffatome enthält, wobei die Gesamtmenge der vorhandenen Diester 20 - 40 Gewichtsprozent beträgt und

(d) wenigstens eine ungesättigte Carbonsäure mit 3 - 5 Kohlenstoffatomen, wobei die Gesamtmenge der ungesättigten Carbonsäure bis zu 5 Gewichtsprozent beträgt, wobei das Polymere in Anwesenheit eines vinylhaltigen oberflächenaktiven Mittels gebildet wird und das Polymere eine Glasübergangstemperatur von weniger als etwa - 30 °C besitzt und einen Gelgehalt von 50 - 70 Gew.-% des Polymeren aufweist.

2. Druckempfindliches Klebstoffpolymer nach Anspruch 1 in welchem das Alkylacrylat in einer Gesamtmenge von 40 - 50 Gew.-% der das Polymere bildenden Monomeren vorliegt.

3. Druckempfindliches Klebstoffpolymer nach einem der Ansprüche 1 oder 2, in welchem der Vinylester in einer Gesamtmenge von 20 - 25 Gew.-%, bezogen auf das Gesamtgewicht der das Polymere bildenden Monomeren, vorliegt.

4. Druckempfindliches Klebstoffpolymer nach einem der Ansprüche 1 - 3, in welchem der Vinylester Vinylacetat ist.

5. Druckempfindliches Klebstoffpolymer nach einem der vorausgehenden Ansprüche, in welchem der Diester der ungesättigten Dicarbonsäure unabhängig 8 - 12 Kohlenstoffatome in jeder Alkylgruppe enthält.

6. Druckempfindliches Klebstoffpolymer nach einem der vorausgehenden Ansprüche, in welchem der Diester der ungesättigten Dicarbonsäure ausgewählt ist aus der Gruppe bestehend aus Di-2-äthylhexylmaleat, Di-2-äthylhexylfumarat und Mischungen derselben.

7. Druckempfindliches Klebstoffpolymer nach einem der vorausgehenden Ansprüche, in welchem die ungesättigte Carbonsäure in einer Menge von 1 - 3 Gew.-% der das Polymer bildenden Gesamtmonomeren vorliegt.

8. Druckempfindliches Klebstoffpolymer nach einem der vorausgehenden Ansprüche, in welchem die ungesättigte Carbonsäure Acrylsäure, Methacrylsäure oder Mischungen derselben ist.

9. Inhärent klebendes druckempfindliches Klebstoffpolymer nach Anspruch 1, welches auf polymerisierter Basis enthält: 48 Gew.-% 2-Äthylhexylacrylat, 21 Gew.-% Vinylacetat, 29 Gew.-% Di-2-äthylhexylmaleat, 1 Gew.-% Acrylsäure und 1 Gew.-% Methacrylsäure.

10. Druckempfindliches Klebstoffpolymer nach einem der vorausgehenden Ansprüche, in welchem ein chelatisierendes Monomer mit wenigstens einer aktiven Methylengruppe in dem Polymer vorhanden ist.

11. Druckempfindliches Klebstoffpolymer nach Anspruch 10, in welchem das chelatisierende Monomer in einer Menge von bis zu einem Gewichtsprozent der das Polymere bildenden Monomeren vorhanden ist.

12. Druckempfindliches Klebstoffpolymer nach Anspruch 10 oder 11, in welchem das chelatisierende Monomer Acetoacetoxyäthylmethacrylat ist.

13. Druckempfindliches Klebstoffpolymer nach einem der vorausgehenden Ansprüche, in welchem das reaktionsfähige oberflächenaktive Mittel Natriumvinylsulfonat, Natriumstyrolsulfonat oder Mischungen derselben darstellt und das reaktionsfähige oberflächenaktive Mittel in einer Menge von bis zu 0,4 Gew.-%, bezogen auf das Gesamtgewicht der das Polymere bildenden Monomeren, vorhanden ist.



14. Druckempfindliches Klebstoffpolymer nach einem der vorausgehenden Ansprüche, in welchem das oberflächenaktive Mittel in einer Menge von 0,1 - 0,25 Gew.-%, bezogen auf die gesamten das Polymere bildenden Monomeren, vorhanden ist.

15. Druckempfindliches Klebstoffpolymer nach einem der vorausgehenden Ansprüche, in welchem das Polymer in Anwesenheit eines Kettenübertragungsmittels gebildet ist.

16. Verfahren zur Erzeugung von inhärent klebenden, druckempfindlichen Klebstoffemulsionspolymeren nach einem der Ansprüche 1 - 15, welches umfaßt:

Unterwerfen einer emulgierten Mischung von Monomeren, die enthält:

(i) wenigstens ein Alkylacrylat mit 4 - 8 Kohlenstoffatomen in der Alkylgruppe, die in einer Gesamtmenge von 35 - 65 Gew.-% der das Polymere bildenden Monomeren vorhanden ist;

(ii) wenigstens einen Vinylester, der 2 - 16 Kohlenstoffatome in der Alkylkette der Säure aufweist, wobei die gesamten Vinylester in einer Menge von 15 - 35 Gew.-% der das Polymere bildenden Monomeren vorhanden sind;

(iii) wenigstens einen Diester einer ungesättigten Dicarbonsäure, der in einer Gesamtmenge von 20 - 35 Gew.-% der das Polymere bildenden Monomeren vorhanden ist, wobei jeder Diester unabhängig 8 - 16 Kohlenstoffatome in der Alkylgruppe des Esters aufweist und

(iv) bis zu 5 Gew.-% der das Polymere bildenden Monomere von wenigstens einer ungesättigten Carbonsäure;

(v) 0 - 10 Gew.-% der das Polymere bildenden Monomeren von wenigstens einem chelatisierenden Monomeren der Emulsionspolymerisation in Anwesenheit eines vinylhaltigen oberflächenaktiven Mittels durch Initiierung der Polymerisation einer anfänglichen Polymermischung, bestehend aus bis zu 10 Gew.-% der Gesamtmonomeren in Anwesenheit eines Initiators und Zugabe des Restes der Monomeren und des Initiators dafür zu dem Emulsionsreaktionssystem innerhalb einer Periode von 4 bis 5 Stunden zur Erzielung eines Gesamtfeststoffgehaltes bis zu 60 Gew.-% der Emulsion, wobei die Emulsionsreaktion unter autogenen Bedingungen bei einer Temperatur von 70 - 85 °C und einem pH-Wert von 2 - 4 in Anwesenheit eines Stabilisatorsystems aufrechterhalten wird, welches ein anionisches und ein nicht ionisches oberflächenaktives System umfaßt, in welchem das Verhältnis von anionischem zu nicht ionischem oberflächenaktiven Mittel 3 : 1 beträgt und das Polymere einen Gelgehalt von 50 - 70 Gew.-% aufweist.

Revendications

1. Polymère adhésif sensible à la pression et autocollant, forme par polymérisation en émulsion, lequel polymère comprend, en considérant sa composition à l'état polymérisé et sur la base du poids total des monomères le constituant,

(a) au moins un acrylate d'alkyle contenant 4 à 8 atomes de carbone dans le groupement alkyle, la part totale des acrylates d'alkyle présents étant comprise entre 35 et 60% en poids;

(b) au moins un ester vinylique contenant 2 à 16 atomes de carbone dans le groupement alkyle de l'acide, la part totale des esters vinyliques présents étant comprise entre 15 et 35% en poids;

(c) au moins un diester d'un acide dicarboxylique insature, dans lequel chaque groupement alkyle du diester contient indépendamment 6 à 12 atomes de carbone, la part totale des diesters présents étant comprise entre 20 et 40% en poids: et

(d) au moins un acide carboxylique insaturé contenant 3 à 5 atomes de carbone, la part totale des acides carboxyliques insaturés présents pouvant aller jusqu'à 5% en poids,

ledit polymère étant formé en présence d'un tensioactif contenant des groupements vinyle, ledit polymère avant une température de transition vitreuse inférieure à -30 °C environ et une teneur en gel de 50 à 70% en poids du polymère.

2. Polymère adhésif sensible à la pression selon la revendication 1, dans lequel l'acrylate d'alkyle est présent dans une quantité totale de 40 à 50% en poids des monomères constituant le polymère.

3. Polymère adhésif sensible à la pression selon la revendication 1 au 2, dans lequel l'ester vinylique est présent dans une quantité totale de 20 à 25% en poids par rapport au poids total des monomères constituant le polymère.



4. Polymère adhésif sensible à la pression selon l'une quelconque des revendications 1 à 3, dans lequel l'ester vinylique est l'acétate de vinyle.
5. Polymère adhésif sensible à la pression selon l'une quelconque des revendications 1 à 4, dans lequel le diester de l'acide dicarboxylique insaturé contient 8 à 12 atomes de carbone dans chaque groupement alkyle considéré indépendamment.
6. Polymère adhésif sensible à la pression selon l'une quelconque des revendications 1 à 5, dans lequel le diester de l'acide dicarboxylique insaturé est choisi dans le groupe constitué par le di-(2-éthylhexyl)-maléate, le di-(2-éthylhexyl)-fumarate et des mélanges de ceux-ci.
7. Polymère adhésif sensible à la pression selon l'une quelconque des revendications 1 à 6, dans lequel l'acide carboxylique insaturé est présent dans une proportion de 1 à 3% en poids du total des monomères constituant le polymère.
8. Polymère adhésif sensible à la pression selon l'une quelconque des revendications 1 à 7, dans lequel l'acide carboxylique insaturé est l'acide acrylique, l'acide méthacrylique ou des mélanges de ceux-ci.
9. Polymère adhésif sensible à la pression et autocollant selon la revendication 1, comprenant, sur la base de sa composition à l'état polymérisé, 48% en poids d'acrylate de 2-éthylhexyle, 21% en poids d'acétate de vinyle, 29% en poids de di-(2-éthylhexyl)-maléate, 1% en poids d'acide acrylique et 1% d'acide méthacrylique.
10. Polymère adhésif sensible à la pression selon l'une quelconque des revendications 1 à 9, dans lequel un monomère chélateur, renfermant au moins un groupement méthylène actif, est présent dans le polymère.
11. Polymère adhésif sensible à la pression selon la revendication 10, dans lequel le monomère chélateur est présent dans une proportion pouvant aller jusqu'à 1% en poids des monomères constituant le polymère.
12. Polymère adhésif sensible à la pression selon la revendication 10 ou 11, dans lequel le monomère chélateur est le méthacrylate d'acéto-acétoxyéthyle.
13. Polymère adhésif sensible à la pression selon l'une quelconque des revendications 1 à 12, dans lequel le tensio-actif réactif est le vinylsulfonate de sodium, le styrènesulfonate de sodium ou des mélanges de ceux-ci, et le tensio-actif réactif est présent dans une proportion pouvant aller jusqu'à 0,4% en poids par rapport au poids total des monomères constituant le polymère.
14. Polymère adhésif sensible à la pression selon l'une quelconque des revendications 1 à 13, dans lequel le tensio-actif réactif est présent dans une proportion de 0,1 à 0,25% en poids du total des monomères constituant le polymère.
15. Polymère adhésif sensible à la pression selon l'une quelconque des revendications, le polymère étant formé en présence d'un agent de transfert de chaîne.
16. Procédé de préparation en émulsion de polymères adhésifs sensibles à la pression et autocollants selon l'une quelconque des revendications 1 à 15, comprenant l'opération consistant:
à soumettre un mélange émulsionné de monomères comprenant:
 - (i) au moins un acrylate d'alkyle contenant 4 à 8 atomes de carbone dans le groupement alkyle et présent dans une proportion totale de 35 à 65% en poids des monomères constituant le polymère;
 - (ii) au moins un ester vinylique contenant 2 à 16 atomes de carbone dans la chaîne alkyle de l'acide, le total des esters vinyliques étant présent dans une proportion de 15 à 35% en poids des monomères constituant le polymère;
 - (iii) au moins un diester d'un acide dicarboxylique insaturé, présent dans une proportion totale de 20 à 35% en poids des monomères constituant le polymère, chaque diester contenant indépendamment 8 à 16 atomes de carbone dans le groupement alkyle de l'ester;



(iv) au moins un acide carboxylique insaturé, dans une proportion allant jusqu'à 5% en poids des monomères constituant le polymère: et:

(v) au moins un monomère chélateur, dans une proportion de 0 à 10% en poids des monomères constituant le polymère,

à une polymérisation en émulsion en présence d'un tensio-actif contenant des groupements vinyle, en amorçant la polymérisation d'un mélange initial de monomères, constituant jusqu'à 10% des monomères totaux en présence d'un amorceur, et en ajoutant le reste des monomères et l'initiateur pour ceux-ci au système de réaction en émulsion en une période de 4 à 5 h pour atteindre une teneur totale en matières solides allant jusqu'à 60% en poids de l'émulsion, ladite réaction en émulsion étant maintenue dans des conditions autogènes à une température de 70 à 85 °C et à un pH de 2 à 4, en présence d'un système stabilisant comprenant un système de tensio-actifs anionique et non ionique dans lequel le rapport du tensio-actif anionique au tensio-actif non ionique est de 3 à 1, ledit polymère ayant une teneur en gel de 50 à 70% en poids.