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(71) Applicants: **DOW GLOBAL TECHNOLOGIES LLC** [US/US]; 2040 Dow Center, Midland, Michigan 48674 (US). **DOW SILICONES CORPORATION** [US/US]; 2200 West Salzburg Road, Midland, Michigan 48686-0994 (US).

(72) Inventors; and

(71) Applicants *(for SC only)*: **HU, Minbiao** [CN/CN]; No. 936 Zhang Heng Road, Shanghai Pilot Free Trade Zone, Shanghai 201203 (CN). **SUN, Tong** [CN/CN]; No. 936 Zhang Heng Road, Shanghai Pilot Free Trade Zone, Shanghai 201203 (CN). **JIANG, Jingui** [CN/CN]; No. 936 Zhang Heng Road, Shanghai Pilot Free Trade Zone, Shanghai 201203 (CN). **PAN, Shi** [CN/CN]; No. 936 Zhang Heng Road, Shanghai Pilot Free Trade Zone, Shanghai 201203 (CN). **FENG, Shaoguang** [US/CN]; No. 936 Zhang Heng Road, Shanghai Pilot Free Trade Zone, Shanghai 201203 (CN). **ZHAI, Xuemei** [CN/CN]; No. 936 Zhang Heng Road, Shanghai Pilot Free Trade Zone, Shanghai 201203 (CN).

(74) Agent: **SHANGHAI PATENT & TRADEMARK LAW OFFICE, LLC**; 435 Guiping Road, Shanghai 200233 (CN).

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(54) Title: FORMALDEHYDE FREE ADHESIVE COMPOSITION

(57) Abstract: A formaldehyde free adhesive composition and a plywood obtained by the adhesive composition is provided, and the plywood retains desired performances, such as water resistance and workability.

Formaldehyde Free Adhesive Composition

FIELD OF THE INVENTION

The present disclosure relates to an aqueous adhesive composition, in particular a formaldehyde free adhesive composition for plywood.

INTRODUCTION

Plywood is a sheet material manufactured from thin layers or "plies" of wood veneer that are glued together with adjacent layers. It is an engineered wood from the family of wood-based panel which includes fiberboard and particle board (chipboard).

Adhesive is used to glue wood layers together to manufacture plywood. The majority of adhesives used are formaldehyde-based curing formulations, such as urea formaldehyde (UF) resin, melamine formaldehyde (MF) resin and phenol formaldehyde (PF) resin. Although several formaldehyde free curing formulations (such as emulsion polymer-isocyanate adhesive (EPI)) exist, they suffer from significant drawbacks such as:

- Short work window. Higher reactivity and fast curing speed result in short work window, i.e., a worker has to use an adhesive as fast as possible, after opening a package of the adhesive. In certain cases, it would require additional investment on new equipment and working process redesign to accommodate such short work window.

- High cost. Diphenylmethane diisocyanate (MDI) or hexamethylene diisocyanate (HDI)-based polyisocyanate raw materials are more expensive than PF/ME/UF-based adhesive packages.

Recently some biomaterial-based adhesive systems such as flour-based or soybean-based adhesives were reported to be used for plywood, but they all show poor performance in workability and water-resistance.

Governmental regulations are pushing towards even lower allowable formaldehyde emission levels for the wood based panel industry (E0 <=0.5mg/L vs. E1 <=1.5mg/L, in which E0 and E1 both refer to the formaldehyde emission standard in China, GB/T 18102-2007), and the public is becoming more and more aware of health hazards posed by formaldehyde such as irritation, allergy and even cancer and malformation. Currently in US, there is a certification for no-added formaldehyde (NAF) product manufacturers by the California Air Resources Board (CARB). In China, an industry association standard of biomaterial-based composite panels and final products of no-added formaldehyde has been recently launched. Therefore,

there is a strong need in the wood-based panel industry for alternative formaldehyde free adhesive compositions for plywood that have desirable performances such as water resistance and good workability.

SUMMARY OF THE INVENTION

The present disclosure provides a novel formaldehyde free adhesive composition for plywood that has desirable performances, such as water resistance and good workability.

In a first aspect, the present disclosure provides a formaldehyde free adhesive composition comprising:

(a) an aqueous emulsion of acrylic polymer;

(b) one or more epoxy compound dispersions or acrylic-epoxy hybrid dispersions;

(c) at least one water soluble, water emulsifiable or water dispersible epoxy curing agent selected from the group consisting of polyamines, polyamides, amidoamines, carboxylic functional polyesters, carboxylic functional polyacrylates, anhydrides, mercaptans, polymercaptans, cyclic amidines, and combinations thereof; and

(d) an aqueous continuous phase;

wherein said acrylic polymer has at least one structural unit of one or more ethylenically unsaturated monomers carrying at least one adhesion prompting function group, and said acrylic polymer has a glass transition temperature of -40℃ to 15℃.

In a second aspect, the present disclosure provides a method for producing plywood, comprising:

(a) providing a formaldehyde free adhesive composition according to this disclosure;

(b) providing two or more layers of wood;

(c) applying the formaldehyde free adhesive composition onto one or two surfaces of said two or more layers of wood;

(d) stacking two or more layers of wood and pressing the stacked two or more layers of wood at room temperature; and

(e) pressing the stacked two or more layers of wood at an elevated temperature of 50-200℃.

In a third aspect, the present disclosure provides a plywood obtained by a formaldehyde free adhesive composition according to the present disclosure.

DETAILED DESCRIPTION OF THE INVENTION

As disclosed herein, the term "composition", "formulation" or "mixture" refers to a physical blend of different components, which is obtained by mixing simply different components by a physical means.

As disclosed herein, the term "formaldehyde free" means that the composition has no added formaldehyde and/or no added formaldehyde generators.

As disclosed herein, the term "glass transition temperature" or "Tg" is determined by differential scanning calorimetry (DSC).

As disclosed herein, the term "alkyl" or "alkoxy" refers to an alkyl or alkoxy having 1 to 20 carbon atoms, preferably 1-10 carbon atoms, more preferably, 1-6 carbon atoms.

The present disclosure provides a novel formaldehyde free adhesive composition for plywood, while retaining desirable performances, such as water resistance and good workability. The adhesive composition may be used to produce cost-effectively plywood, without impacting current manufacture process. The formaldehyde free adhesive composition according to the present disclosure is also free of polyisobutylene compounds, vinyl acetate-based polymers and polymers comprising 80 weight-percent or more ethylenically unsaturated acid co-monomers.

The present disclosure provides a formaldehyde free adhesive composition comprising:

(a) an aqueous emulsion of acrylic polymer;

(b) one or more epoxy compound dispersions or acrylic-epoxy hybrid dispersions;

(c) at least one water soluble, water emulsifiable or water dispersible epoxy curing agent selected from the group consisting of polyamines, polyamides, amidoamines, carboxylic functional polyesters, carboxylic functional polyacrylates, anhydrides, mercaptans, polymercaptans, cyclic amidines, and combinations thereof; and

(d) an aqueous continuous phase;

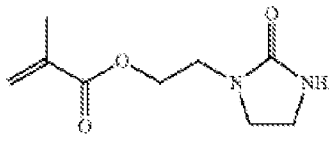
wherein said acrylic polymer has at least one structural unit of one or more ethylenically unsaturated monomers carrying at least one adhesion prompting function group, and said acrylic polymer has a glass transition temperature of -40℃ to 15℃.

The aqueous emulsion of acrylic polymer can be prepared through free radical emulsion or suspension addition polymerization or by dispersion of a pre-formed polymer under shear into an aqueous medium. Monomers suitable for the preparation of the acrylic polymer include, but are not limited to, (meth)acrylic acid and (meth)acrylates, such as alkyl

(meth)acrylates. Examples of alkyl (meth)acrylates are, but not limited to, methyl acrylate, ethyl acrylate, butyl acrylate, glycidyl methacrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, and 2-ethylhexyl methacrylate, and combinations thereof.

The acrylic polymer may further comprise structural units of one or more styrene monomers. The styrene monomers may include, for example, styrene, substituted styrene, or mixtures thereof. The substituted styrene may include, for example, benzyl acrylate, 2-phenoxyethyl acrylate, butylstryene, methylstyrene, p-methoxystyrene, or mixtures thereof. Preferred styrene monomer is styrene. The polymer may comprise, by weight of the polymer, 5% or more, 10% or more, 15% or more, 17% or more, 19% or more, or even 21% or more, and at the same time, 40% or less, 35% or less, 30% or less, 28% or less, or even 26% or less, of structural unit(s) of the styrene monomer(s).

The acrylic polymer in the present disclosure may comprise structural units of one or more ethylenically unsaturated monomers carrying at least one adhesion prompting function group. The adhesion prompting function group may be selected from the group consisting of ureido, alkoxysilane (preferably hydrolyzable alkoxysilane), nitrile, hydroxyl, or phosphorous groups. Suitable ureido functional monomer includes, for example, ureido group containing (meth)acrylic acid alkyl esters. Examples of suitable ureido monomers are illustrated below: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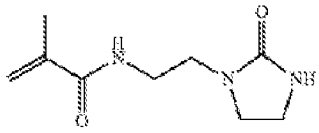
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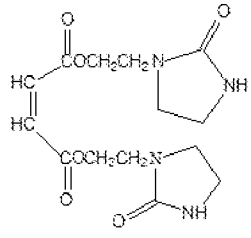
, or mixtures thereof. Suitable alkoxysilane functional monomer includes, for example, vinyltrialkoxysilanes such as vinyltrimethoxysilane; alkylvinyldialkoxysilanes; (meth)acryloxyalkyltrialkoxysilanes such as (meth)acryloxyethyltrimethoxysilane and (meth)acryloxypropyltrimethoxysilane; derivatives thereof, and combinations thereof. Suitable nitrile functional monomer includes, for example, (alkyl)acrylonitrile, such as (meth)acrylonitrile. Suitable hydroxyl functional monomer includes, for example, hydroxy-functional (meth)acrylic acid alkyl ester such as hydroxyethyl methacrylate and hydroxypropyl methacrylate, or mixtures thereof. Suitable phosphorous functional monomer includes, for

example, phosphorous-containing (meth)acrylates, such as phosphoethyl (meth)acrylate, phosphopropyl (meth)acrylate, phosphobutyl (meth)acrylate, salts thereof, and mixtures thereof; $CH_2=C(R)-C(O)-O-(R_1O)_n-P(O)(OH)_2$, wherein R=H or CH_3, R_1=alkyl, and n=2-6, such as SIPOMER PAM-100, SIPOMER PAM-200, and SIPOMER PAM-300 all available from Solvay; phosphoalkoxy (meth)acrylates such as phospho ethylene glycol (meth)acrylate, phospho di-ethylene glycol (meth)acrylate, phospho tri-ethylene glycol (meth)acrylate, phospho propylene glycol (meth)acrylate, phospho di-propylene glycol (meth)acrylate, phospho tri-propylene glycol (meth)acrylate, salts thereof, and mixtures thereof. The acrylic polymer may comprise, based on the weight of the polymer, from 0.1% to 20% by weight, from 0.3% to 10% by weight, from 0.5% to 5% by weight, or from 1% to 3% by weight, of structural units of structural units of one or more ethylenically unsaturated monomers carrying at least one functional group.

The acrylic polymer in the present disclosure may comprise structural units of one or more additional monomers. The additional monomers include, but not limited to, itaconic acid, or fumaric acid; or a monomer bearing an acid-forming group which yields or is subsequently convertible to, such an acid group (such as anhydride, (meth)acrylic anhydride, or maleic anhydride); p-styrenesulfonic acid sodium salt (SSS); acrylamide; or mixtures thereof.

The acrylic polymer in the present disclosure may have a weight average molecular weight of from 10,000 to 1,000,000, from 20,000 to 200,000, or from 40,000 to 150,000. The weight average molecular weight may be measured by gel permeation chromatography (GPC) calibrated by the polystyrene standard.

The acrylic polymer in the present disclosure has a glass transition temperature of -40℃ to 15℃, preferably, -40℃ to 10℃, more preferably -40℃ to 7℃.

In one embodiment, the aqueous emulsion of acrylic polymer is PRIMAL™ EC2848ER, ELASTENE™ 2468M, PRIAML™ AC261p, MAINCOTE™ PR-71K, PRIMAL™ SF-155, ROBOND™ PS-90, PRIMAL™ EC-2540, ELASTENE™ 2468, PRIMAL™ EC-2949, PRIMAL™ EC-4811, PRIMAL™ EC-4642 ME, PRIMAL™ EC-1791, ROBOND™ L-168, TIANBA™ 2012, ELASTENE™ 2475, available from The Dow Chemical Company.

In the adhesive composition of the present disclosure, component (a) comprises 5-70%, preferably, 10-60%, more preferably, 20-50% by weight of the composition, based on the

solids of the composition.

Examples of suitable epoxy compounds include, but are not limited to aliphatic epoxy resins, cyclo-aliphatic epoxy resins, and aromatic epoxy resins. More specific examples include, but are not limited to, 1,2-propanediol diglycidyl ether, 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, poly(propylene glycol) diglycidyl ether, 1,4-cyclohexanedimethanol diglycidyl ether, 1,3-cyclohexanedimethanol diglycidyl ether, 3',4'-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, 3,4-epoxycyclohexyloxirane, 2-(3',4'-epoxycyclohexyl)-5,1"-spiro-3",4"-epoxycyclohexane-1,3-dioxane, vinyl cyclohexene monoxide, bis(3,4-epoxycyclohexylmethyl) adipate, the diglycidyl ester of phthalic acid, the diglycidyl ester of hexahydrophthalic acid, diglycidyl ether of bisphenol A (DGEBA), solid epoxy resins based on DGEBA, phenoxy resins, the diglycidyl ether of bisphenol F, an epoxy novolac resin, cresol epoxy novolacs, and mixtures thereof. Preferably, a method to prepare an epoxy compound dispersion is to mix an epoxy compound with water to form an epoxy dispersion, wherein the epoxy compound dispersion comprises epoxy particles having a size in the range of from 50 nanometers to 10 microns. In various embodiments, the mixing occurs at a temperature in the range of from 10°C to 90°C, preferably from 20°C to 60°C, and a high-speed mixer or a homogenizer is used. In various embodiments, surfactants may be used in the preparation of the epoxy compound dispersion. Suitable surfactants include, but are not limited to, nonionic surfactants, such as APEO free; nonionic wetting agents such as polyalkylene oxide block copolymers, polyoxyethylene glycol alkyl ethers, glucoside alkyl ethers, fatty acid esters, glycerol alkyl esters, sorbitan alkyl esters, and polyoxyethylene glycol alkylphenol ethers. The preferred nonionic wetting agents include commercially available wetting agents such as TRITON™ X-405 Octylphenol Ethoxylate available from The Dow Chemical Company. If a surfactant is used, it is generally used at a concentration in the range of from 0.5 weight percent to 5 weight percent. Preferred epoxy compound dispersion is XCM-38 available from The Dow Chemical Company.

Examples of suitable acrylic-epoxy hybrid include, but not limited to, those disclosed in WO2017112018A1. In one embodiment, the acrylic-epoxy hybrid is prepared by mixing the above-mentioned epoxy compound dispersion with an acrylate dispersion to form an acrylic/epoxy latex having acrylic particles fully imbibed with epoxy. This mixing typically occurs at a temperature in the range of from 20℃ to 80℃, preferably from 40℃ to 60℃. The

acrylate dispersion can be prepared through free radical emulsion or suspension addition polymerization or by dispersion of a pre-formed polymer under shear into an aqueous medium. Monomers suitable for the preparation of the acrylate dispersion include, but are not limited to, acrylates and methacrylates, such as methyl acrylate, ethyl acrylate, butyl acrylate, glycidyl methacrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, and 2-ethylhexyl methacrylate, and combinations thereof. Preferred acrylic-epoxy hybrid is Ecoground™ AEH-2014 available from The Dow Chemical Company.

In the adhesive composition of the present disclosure, component (b) comprises 3-50%, preferably, 5-40%, more preferably, 10-20% by weight of the composition, based on the solids of the composition.

The adhesive composition according to the present disclosure may further comprise a rheology modifier. The rheology modifier may include, not limited to, a non-ionic urethane polymer, cellulose, polyethylene glycol, starch ether, polyvinyl alcohol, polyimide, gum, flour and mixtures thereof. The rheology modifier may be present, based on the total solid weight of the adhesive composition, in an amount of generally from 0.1 to 5.0% by weight, from 0.2% to 3% by weight, or from 0.5% to 2.0% by weight.

The adhesive composition according to the present disclosure may further comprise one or more defoamers. "Defoamers" herein refer to chemical additives that reduce and hinder the formation of foam. Defoamers may be silicone-based defoamers, mineral oil-based defoamers, ethylene oxide/propylene oxide-based defoamers, or mixtures thereof. Suitable commercially available defoamers include, for example, TEGO Airex 902 W and TEGO Foamex 1488 polyether siloxane copolymer emulsions both available from TEGO, BYK-024 silicone deformer available from BYK, NOPCO® NXZ deformer available from NOPCO or mixtures thereof. The defoamer may be present, by weight of the total solid of the adhesive composition, in an amount of generally from 0.1 to 2%, from 0.2% to 1.5%, or from 0.5% to 1.0%.

The adhesive composition according to the present disclosure may further comprise one or more fillers. The fillers may include, but not limited to, calcium carbonate, silica, silicate, gypsum, pulp, wood powder, flour powder and mixtures thereof. The filler may be present, by weight of the total solid of the adhesive composition, in an amount of generally from 1 to 75%, from 10% to 70%, or from 20% to 60%, or from 30 to 60%.

The adhesive composition according to the present disclosure may further comprise at least one water soluble, water emulsifiable or water dispersible epoxy curing agent. Examples of suitable curing agents include, but are not limited to, polyamines, polyamides, amidoamines, carboxylic functional polyesters, carboxylic functional polyacrylates, anhydrides, mercaptans, polymercaptans, cyclic amidines, and combinations thereof. More specific examples include, but are not limited to diethylenetriamine, triethylenetetramine, tetraethylenepentamine, 2,2,4-trimethylhexamethylenediamine, 2,4,4-trimethylhexamethylenediamine, 1,6-hexanediamine, l-ethyl-l,3-propanediamine, bis(3-aminopropyl) piperazine, N-aminoethylpiperazine, N,N-bis(3-aminopropyl)ethylenediamine, 2,4-toluenediamine, 2,6-toluenediamine, 1,2-diaminocyclohexane, l,4-diamino-3,6-diethylcyclohexane, l,2-diamino-4-ethylcyclohexane, l,4-diamino-3,6-diethylcyclohexane, 1 -cyclohexyl-3 ,4-diaminocyclohexane, isophorone-diamine, norboranediamine, 4,4'-diaminodicyclohexylmethane, 4,4'-diaminodicyclohexylmethane, 4,4'-diaminodicyclohexyl-propane, 2,2-bis(4-aminocyclohexyl)propane, 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane, 3-amino-l-cyclohexane-amino-propane, 1,3- and 1,4-bis(aminomethyl)cyclohexane, m-xylylenediamine, p-xylylenediamine, polyoxypropylenediamines, polyamidoamines, and aminoplast resins formed by the reaction of ureas and melamines with aldehydes. In the adhesive composition of the present disclosure, the amount of the curing agent depends on the epoxy dosage. The active hydrogen of the curing agent to epoxy stoichiometry ratio is from 0.25 to 2, preferably 0.5-1.5, more preferably, 0.8-1.2. Generally, the curing agent may be present, by weight of the total solid of the adhesive composition, in an amount of from 0.5 to 20%, from 1% to 15%, or from 1% to 10%, or from 1 to 8%.

In addition to the components described above, the adhesive composition of the present invention may further comprise any one or combination of the following additives: dispersant buffers, neutralizers, humectants, mildewcides, biocides, colorants, flowing agents, crosslinkers, anti-oxidants, plasticizers, leveling agents, thixotropic agents, adhesion promoters, and grind vehicles. In one embodiment, the additive is selected from the group consisting of silane and isocyanate prepolymer. When present, these additives may be present in a combined amount of from 0 to 5% by weight or from 0.1% to 3% by weight, or from 0.5 to 1.5% by weight, based on the total solid weight of the adhesive composition.

In a second aspect, the present disclosure provides a method for producing plywood, comprising:

(a) providing a formaldehyde free adhesive composition according to this disclosure;

(b) providing two or more layers of wood;

(c) applying the formaldehyde free adhesive composition onto one or two surfaces of said two or more layers of wood;

(d) stacking two or more layers of wood and pressing the stacked two or more layers of wood at room temperature; and

(e) pressing the stacked two or more layers of wood at an elevated temperature of 50-200℃.

The plywood obtained by the above method generally comprises, not limited to, 3-11 layers of wood, preferably, 5-9 layers of wood, more preferably 5-7 layers of wood.

In the above step (d), the pressing is carried out at a preferred pressure of 0.5-20MPa, more preferably 1-10MPa, most preferably 1-5MPa.

In the above step (d), the pressing is carried out for 1-120 minutes, preferably 10-80 minutes, and more preferably 20-40 minutes.

In the above step (e), the pressing is carried out at a preferred pressure of 0.5-20MPa, more preferably 1-10MPa, most preferably 1-5MPa.

In the above step (e), the pressing is carried out at a preferred temperature of 60-180℃, more preferably 80-150℃, most preferably 100-120℃.

In the above step (e), the pressing is carried out for 1-80 minutes, preferably 5-40 minutes, and more preferably 10-20 minutes.

In a third aspect, the present disclosure provides a plywood obtained by a formaldehyde free adhesive composition according to the present disclosure.

EXAMPLES

Some embodiments of the invention will now be described in the following Examples, wherein all parts and percentages are by weight unless otherwise specified.

Table 1. Raw materials

Function	Ingredients	Supplier
Acrylic emulsion	PRIMAL™ EC2848ER	The Dow Chemical Company
	ELASTENE™ 2468M	
	PRIMAL™ AC261p	
	MAINCOTE™ PR-71K	
	PRIMAL™ SF-155	
	ROBOND™ PS-90	
	PRIMAL™ EC-2540	
	ELASTENE™ 2468	
	PRIMAL™ EC-2949	
	PRIMAL™ EC-4811	
	PRIMAL™ EC-4642 ME	
	PRIMAL™ EC-1791	
	ROBOND™ L-168	
	TIANBA™ 2012	
	ELASTENE™ 2475	
Epoxy dispersion	XCM-38	
Acrylic-epoxy dispersion	Ecoground™ AEH-2014	
Filler	Calcium carbonate	Changxing Qingsheng Calcium Industry Co., LTD
	Industry flour	Wujiang Junfa Chemical Co., LTD
Rheology modifier	Acrysol™ RM-8W	The Dow Chemical Company
Defoamer	NOPCO® NXZ	NOPCO
Additive	3-Aminopropyltriethoxysilane (KH550)	SCRC

	γ -(2,3-epoxypropoxy)propyltrimethoxysilane (KH560)	
Hardener	Aradur® 36 BD	Huntsman
	Pentaethylenehexamine	TCI

Glass transition temperature measurements

10 grams of emulsion were placed in a plastic dish and allowed to dry for 24 hours at room temperature. The resultant film was then subjected to 50°C for 48 hours to further dry the film. A small piece of the film was cut off and placed in a TA Instruments standard aluminum hermetic pan which was sealed. The sample was subjected to two cycles of -60°C to 100°C at a heating ramp rate of 10°C/min. The glass transition temperature for the polymer is measured at the midpoint of the inflection using the half-height method.

Boiling water test

One of the most important requirements of plywood is water resistance. According to the Chinese code GB/T18259-2009, for plywood of class I, it needs to pass boiling water test. A detailed test method is described below according to the Chinese code GB/T17657-2013:

1) Six test samples (75mm*75mm) were cut out from the plywood sample (300mm*300mm).

2) The test samples were immerged into boiling water for 4 hours.

3) Then the test samples were taken out from boiling water and placed in oven (63°C) to dry for 20 hours.

4) Then the dried test samples were immerged into boiling water for another 4 hours.

5) The test samples were taken out and placed in oven (63°C) to dry for 3 hours.

6) Then the interface between different layers was carefully observed. The stripping length of each layer of each sample should be less than 25 mm.

Due to the volume expansion of wood when it absorbed water, it would cause internal stress between different wood layers. So the boiling water test evaluates not only the water resistance performance of adhesive but also the adhesion performance under wet condition. In

lab test, the boiling water test was used to evaluate the performance of the adhesive.

Example 1: Control Example and Inventive Examples

Acrylic emulsion, epoxy or acrylic-epoxy hybrid dispersion and water were mixed together according to the formulation, and defoamer was also added. Filler was added, and dispersed by stirring. Rheology modifier was added to adjust the viscosity to around 20000 cp (Brookfield, 5#, 30rpm). A curing agent was added and dispersed by stirring. Additive (if any) might be added. The adhesive composition was ready to use. The above components and their amounts were listed in Table 2 below

In order to simulate the condition in factory, the adhesive composition waited 4 hours before to be applied on the wood layer surface. After 4 hours, the adhesive was applied on the wood layer (30cm * 30cm). The loading amounts was 200g/m^2. Here the wood was eucalyptus which was widely used in the market. The wood layers with adhesive were left for another 4 hours before they were stacked layer by layer for pressing under room temperature. The stacked wood layers (7 layers) were taken for pressing at room temperature for 40 mins. The pressure was around 2 MPa. Then the stacked wood layers were taken for pressing at 110 ℃. The pressing time was 1 min/mm and the pressure was around 2MPa. The plywood was ready after hot pressing and it was left for another 24 hours at room temperature before it was tested in boiling water for 4 hours. The results of boiling water test of the plywood were listed in Table 2 below.

Table 2. Basic formulation of adhesive and water resistance performance

	Acrylic emulsion /g	Epoxy or acrylic-epoxy hybrid dispersion /g		Filler /g	Curing agent /g		Additive /g		Water /g	Boiling water test
	Elastene™ 2468M	XCM38	Ecoground™ AEH-2014	$CaCO_3$ (700 mesh) /g	Pentaethylenehexamine	Aradur® 36BD	KH550	KH560		
CE-1	120 (35.5%)			110 (64.5%)					20	Failed

IE-1	80 (20.3%)	40 (12.9%)		120 (60.4%)		16 (6.4%)			35	Passed
IE-2	80 (21.2%)	40 (13.4%)		120 (62.8%)	5 (2.6%)				35	Passed
IE-3	80 (22.0%)		40 (11.0%)	120 (65.3%)		4 (1.7%)			35	Passed
IE-4	100 (29.8%)	20 (7.5%)		100 (58.9%)		8 (3.8%)			35	Passed
IE-5	100 (29.7%)	20 (7.5%)		100 (58.9%)		7 (3.3%)	1 (0.6%)		35	Passed
IE-6	100 (29.6%)	20 (7.5%)		100 (58.6%)		8 (3.7%)		1 (0.6%)	35	Passed

CE: Control example

IE: Innovative example

Note: solid content of 2468M is 50.5%, solid content of XCM38 is 64%, solid content of AEH-2014 is 50.5%, solid content of Aradur® 36 BD is 80%. The numbers in the parentheses are the solid content of the materials in the formulation.

If the adhesive composition comprised acrylic emulsion, the water resistance performance was not good enough to pass the boiling water test (CE-1). While the epoxy dispersion or acrylic-epoxy hybrid dispersion was added in the formulation, the adhesive compositions, IE-1 to IE-4, showed good adhesion and water resistance performance. Different amine curing agent could be adopted, like pentaethyleneheamine and Aradur® 36BD (a water emulsifiable amine curing agent). Some additive could also been added, like silane, which could give better performance (IE-5 and IE-6).

Example 2

The IE-4 sample was taken to the Wood Products Quality Test & Inspection Center of State Forestry Administration (Nanjing, China) to evaluate the formaldehyde value. The formaldehyde value was undetectable, which had proved the formaldehyde free concept.

Example 3

In order to further study the factor of acrylic latex which would benefit the adhesive performance, a series of comparison works had been conducted. The formulation of IE-4 had

been used to do the comparison works. First, Tg (glass transition temperature) of the acrylic latex was investigated. If the latex had high Tg, the formulation lost its tackiness under room temperature. It caused cold press problem that the wood layers could not be initially bonded together. If the latex had very low Tg, the formulation would be lack of cohesion performance which would cause final adhesion problem.

Table 3. Acrylic latex Tg evaluation

Acrylic latex	Tg/° C	Cold press performance	Boiling water test
PRIMAL™ AC261p	25	Not good (could be peeled off)	Failed
MAINCOTE™ PR-71K	20.6	Not good (could be peeled off)	Failed
PRIMAL™ SF-155	7.2	Good	Passed
ELASTENE™ 2468M	-19.6	Good	Passed
PRIMAL™ 2848ER	-31.1	Good	Passed
ROBOND™ PS-90	-43	Good	Failed

Example 4

In this example, the functional monomers in the acrylic latex were also carefully evaluated. The results were summarized in Table 4 below. The formulation of IE-4 had been used to do the comparison works. Based on the data below, the functional monomers showed a significant effect on final performance. With similar Tg, when the latexes had a functional monomer(s) they show good mechanical performance.

Table 4. Functional monomer evaluation

Acrylic latex	Functional monomer	Tg/℃	Boiling water test
PRIMAL™ EC-2540	No	-7.4	Failed
ELASTENE™ 2468	Yes	-17.8	Passed
ELASTENE™ 2468M	Yes	-19.6	
PRIMAL™ EC-2949	Yes	-30.8	
PRIMAL™ EC-4811	Yes	-18.8	
PRIMAL™ EC-4642 ME	Yes	-14.4	
PRIMAL™ EC-1791	Yes	-30.4	
ROBOND™ L-168	No	4.7	Failed
PRIMAL™ SF-155	Yes	7.2	Passed
TIANBA™ 2012	No	-10.5	Failed
ELASTENE™ 2475	Yes	-12.1	Passed

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What is claimed is:

1. A formaldehyde free adhesive composition comprising:

(a) an aqueous emulsion of acrylic polymer;

(b) one or more epoxy compound dispersions or acrylic-epoxy hybrid dispersions;

(c) at least one water soluble, water emulsifiable or water dispersible epoxy curing agent selected from the group consisting of polyamines, polyamides, amidoamines, carboxylic functional polyesters, carboxylic functional polyacrylates, anhydrides, mercaptans, polymercaptans, cyclic amidines, and combinations thereof; and

(d) an aqueous continuous phase;

wherein said acrylic polymer has at least one structural unit of one or more ethylenically unsaturated monomers carrying at least one adhesion prompting function group, and said acrylic polymer has a glass transition temperature of -40℃ to 15℃.

2. The adhesive composition according to claim 1, wherein the adhesion prompting function group is selected from the group consisting of ureido, alkoxysilane, nitrile, hydroxyl, and phosphorous groups.

3. The adhesive composition according to claim 1, wherein the acrylic polymer has a glass transition temperature of -40℃ to 10℃.

4. The adhesive composition according to claim 1, wherein the one or more epoxy compound dispersions are independently selected from the group consisting of cyclo-aliphatic epoxy resin dispersions, and aromatic epoxy resin dispersions.

5. The adhesive composition according to claim 1, wherein the acrylic-epoxy hybrid dispersions are prepared by mixing epoxy compound dispersion with an acrylate dispersion to form an acrylic/epoxy latex having acrylic particles fully imbibed with epoxy.

6. The adhesive composition according to claim 1, wherein the adhesive composition further comprises one or more of a filler, a defoamer, a rheology modifier and an additive.

7. The adhesive composition according to claim 1, wherein the adhesive composition comprises the following components:

1) 10-70% of an aqueous emulsion of acrylic polymer,

2) 3-70% of one or more epoxy compound dispersions or acrylic-epoxy hybrid dispersions,

3) 0-75% of a filler,

4) 0.1-2% of defoamer,

5) 0.1-2% of rheology modifier,

6) 0.5-20% of at least one water soluble, water emulsifiable or water dispersible epoxy curing agent,

7) 0-5% of an additive,

8) water,

the above percentages are calculated based on the total solid weight of the adhesive composition.

8. A method for producing plywood, comprising the following steps:

(a) providing a formaldehyde free adhesive composition according to any one of claims 1-6;

(b) providing two or more layers of wood;

(c) applying the formaldehyde free adhesive composition onto one or two surfaces of said two or more layers of wood;

(d) stacking two or more layers of wood and pressing the stacked two or more layers of wood at room temperature; and

(e) pressing the stacked two or more layers of wood at an elevated temperature of 50-200℃.

9. A plywood obtained by a formaldehyde free adhesive composition according to any one of claims 1-7.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2019/077265

A. CLASSIFICATION OF SUBJECT MATTER

C08L 63/00(2006.01)i; C08L 33/08(2006.01)i; C09J 163/00(2006.01)i; C09J 133/08(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08L63; C08L33; C09J163; C09J133

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT,CNKI,DWPI,EPODOC,WANFANG: water, adhesive, epoxy, aqueous, +wood, adhesion, +aldehyde, +acryl+, adhesive?, binder?, emulsion

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5037700 A (NAT STARCH CHEM INVEST) 06 August 1991 (1991-08-06) see EXAMPLE I, column 2, lines 40-57, column 6, lines 18-25, lines 48-54	1-4, 6-9
X	US 5480720 A (ROHM & HAAS) 02 January 1996 (1996-01-02) see EXAMPLE 1-4, column 2, lines 56-65, column 4, lines 34-39, column 6, lines 9-13, column 7, lines 24-29, column 8, lines 13-19	1-4, 6-9
A	CN 109071907 A (DOW GLOBAL TECHNOLOGIES LLC) 21 December 2018 (2018-12-21) see the whole document	1-9
A	CN 102653623 A (ROHM & HAAS CO) 05 September 2012 (2012-09-05) see the whole document	1-9
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A	CN 109251682 A (UNIV BEIJING FORESTRY) 22 January 2019 (2019-01-22) see the whole document	1-9

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
02 December 2019	**12 December 2019**

Name and mailing address of the ISA/CN	Authorized officer
National Intellectual Property Administration, PRC **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing** **100088** **China**	**HE,Yong**
Facsimile No. **(86-10)62019451**	Telephone No. **01062084424**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2019/077265

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