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(54) Title: PACKAGING ADHESIVES BASED ON RENEWABLE RAW MATERIALS

(57) Abstract: The present invention relates to adhesive compositions, in particular packaging adhesives that contain polyester polyols based on betulin and to a method for the preparation thereof. The present invention further relates to a method for bonding film-like substrates, using the described adhesive composition.



Packaging adhesives based on renewable raw materials

[0002] The present invention relates to adhesive compositions, in particular packaging adhesives that contain polyester polyols based on betulin and to a method for the preparation thereof. The present invention further relates to a method for bonding film-like substrates, using the described adhesive composition.

[0003] In the context of growing environmental awareness and the on-going sustainability debate, there is an increasing demand for sustainable packaging solutions based on renewable resources. There is therefore a need for adhesives for packaging of which as high a proportion as possible consists of renewable raw materials. The aim of this is to produce packaging systems having approximately 100% based on renewable raw materials. This should make an important contribution to meeting sustainability goals associated in particular with the buzzword carbon footprint.

[0004] Moreover, as well as the proportion of renewable raw materials, it is desirable to achieve, in particular in food packaging, additionally improved technical properties, for example resistance to aggressive filling materials or, also in the context of saving energy, possible curing of the used adhesive system at room temperature.

[0005] In this context, the spotlight is placed in particular on betulin, a compound from the group of pentacyclic triterpenes.

[0006] WO 2006/053936 describes a method for producing polymers based on biodegradable or substantially renewable raw materials, which can be cross-linked by free radical reaction, betulin being mentioned as a possible diol component.

[0007] In the *Journal of the American Oil Chemists' Society* (JAOCS) dated January 1981 (pages 20 to 23), V. Erä and Jääskeläinen describe a synthesis pathway for preparing fatty acid esters of betulin via the acid chloride.

[0008] In the *Russian Journal of Applied Chemistry*, vol. 78, no. 7, 2005, pages 1162-1165, V.E. Nemilov et al describe a kinetic study on the polycondensation of betulin with adipic acid, the primary focus being in particular on the different behavior of the primary and secondary hydroxyl groups of the betulin and the isopropenyl groups thereof.

[0009] The currently available adhesive systems that contain at least a certain proportion of renewable raw materials have the drawback that they have a lower efficiency compared with conventional systems based on petrochemical raw materials, which is manifested in lower adhesion values and resistance.

[0010] The problem addressed by the present invention is therefore that of providing an adhesive composition that has a high proportion of renewable raw materials and a comparable or improved efficiency compared with conventional systems and is suitable in particular for producing food

packaging.

[0011] It has surprisingly been found that this problem is solved by an adhesive composition that contains a polyester polyol based on betulin and an NCO-terminated compound.

[0012] The present invention therefore firstly relates to an adhesive composition comprising:

- a) at least one polyester polyol based on betulin; and
- b) at least one NCO-terminated compound.

[0013] It has surprisingly been found that, in this manner, an adhesive composition can be provided of which up to 100% can be obtained from renewable raw materials and which has an efficiency that is comparable with respect to conventional adhesive compositions and is even improved in some areas.

[0014] In a preferred embodiment, the polyester polyol used in the adhesive composition according to the invention has a proportion of betulin structural units of from 6 to 65 mol.%, preferably 10 to 50 mol.%.

[0015] The polyester polyol contained in the adhesive composition according to the invention is preferably obtained by reacting betulin and one or more triglycerides. In a preferred embodiment, the triglyceride has at least one free hydroxyl group. In this case, the free hydroxyl group may already be present in the triglyceride or be introduced by functionalization. In another preferred embodiment, the reaction of the betulin with the one or more triglycerides can be carried out in the presence of one or more dicarboxylic acids.

[0016] The composition of the reaction mixture, from which the polyester polyol contained in the adhesive composition according to the invention is obtained, can be adjusted according to the properties of the polyester polyol that are to be achieved, for example its viscosity or its glass transition temperature. However, it has proven advantageous if the proportion of betulin in the reaction mixture is not too large, in order to prevent any problems when processing the raw materials.

[0017] In a particularly preferred embodiment, the polyester polyol of the composition according to the invention is therefore obtained from a reaction mixture that comprises the following monomer units as starting components:

- i) betulin in an amount of from 5 to 50 wt.%, preferably 25 to 35 wt.%; and
- ii) dicarboxylic acid in an amount of from 5 to 45 wt.%, preferably 8 to 40 wt.%; and
- iii) triglyceride in an amount of from 20 to 80 wt.%, preferably 40 to 70 wt.%,

in each case based on the total weight of the monomer units.

[0018] The dicarboxylic acid is preferably a dicarboxylic acid selected from the group consisting of aliphatic dicarboxylic acids having 4 to 24 carbon atoms, aromatic dicarboxylic acids, dimer fatty acids and mixtures and derivatives thereof. The derivatives may be esters, acid chlorides or anhydrides of dicarboxylic acids, for example.

[0019] In a particularly preferred embodiment, the at least one dicarboxylic acid is an aliphatic dicarboxylic acid selected from the group consisting of succinic acid, adipic acid, azelaic acid, sebacic acid, dodecanedioic acid, tetradecandioic acid and mixtures thereof.

[0020] Suitable aromatic dicarboxylic acids are preferably selected from the group consisting of phthalic acid, isophthalic acid, terephthalic acid, furandicarboxylic acid, anhydrides and methyl esters thereof, and mixtures thereof.

[0021] In a preferred embodiment, the dimer fatty acid or dimer fatty acids is/are dimers of fatty acids of the general formula $C_nH_{2n+1}COOH$, where n is an integer from 4 to 33, preferably 7 to 17. In addition to dimer fatty acids, derivatives thereof are preferably also used, which are obtained by hydrogenating or distilling the corresponding dimer fatty acids, for example. Further preferred is the fatty acid selected from the group consisting of caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, the derivatives of these fatty acids and mixtures thereof.

[0022] The at least one triglyceride is preferably selected or derived from a compound selected from the group consisting of soybean oil, linseed oil, sunflower oil, safflower oil, rapeseed oil, physic nut oil, light walnut oil, grapeseed oil, canola oil, corn oil, cashew kernel oil, fish oil, castor oil, tall oil, coconut oil, palm oil, palm kernel oil, olive oil and mixtures thereof. The specified triglyceride is particularly preferably selected from the group consisting of castor oil, soybean oil and derivatives of said compounds. Furthermore, synthetic or biotechnologically prepared triglycerides can also be used.

[0023] The adhesive composition according to the invention further contains an NCO-terminated compound. The NCO-terminated compound is preferably selected from the group consisting of 1,5-naphthylene diisocyanate (NDI), 2,4'- or 4,4'-diphenylmethane diisocyanate (MDI), isomers of toluene diisocyanate (TDI), methylene triphenyl triisocyanate (MIT), hydrogenated MDI (H12MDI), tetramethylxylene diisocyanate (TMXDI), 1-isocyanatomethyl-3-isocyanato-1,5,5-trimethylcyclohexane (IPDI), xylene diisocyanate (XDI), hexane-1,6-diisocyanate (HDI), pentamethylene diisocyanate (PDI) and dicyclohexylmethane diisocyanate, as well as mixtures thereof.

[0024] In a preferred embodiment, the NCO-terminated compound is used in the form of oligomers, in particular trimers, or in the form of polymers. The NCO-terminated compound is particularly preferably used in the form of prepolymers, which are obtained by reacting an excess of a polyisocyanate with a compound carrying OH groups and/or NH groups. The polyisocyanates may

be the above-mentioned polyisocyanates, for example. Polyetheramines can be used as compounds carrying NH groups, for example.

[0025] An embodiment of the present invention in which the compound containing NCO groups is also prepared starting from renewable raw materials is particularly preferred. Compounds such as pentamethylene diisocyanate are therefore particularly preferred. The pentamethylene diisocyanate is preferably used as a trimer.

[0026] The adhesive composition according to the invention has the at least one polyester polyol based on betulin preferably in an amount of from 20 to 90 wt.%, preferably 30 to 80 wt.%, particularly preferably 40 to 60 wt.%, in each case based on the total weight of the solvent-free adhesive composition.

[0027] In a further preferred embodiment, the adhesive composition according to the invention contains the NCO-terminated compound in an amount of from 10 to 80 wt.%, preferably 20 to 70 wt.%, in particular 30 to 60 wt.%, in each case based on the total weight of the solvent-free adhesive composition.

[0028] In a preferred embodiment, the adhesive composition according to the invention has a proportion of renewable raw materials of from 50 to 100 wt.%, preferably 60 to 95 wt.%, in each case based on the total weight of the solvent-free adhesive composition.

[0029] It has surprisingly been found that the adhesive composition according to the invention has a particularly advantageous processability when the ratio of NCO groups to OH groups in the composition is no more than 1 to 6. An embodiment of the adhesive composition according to the invention is therefore preferred in which the adhesive composition has a ratio of NCO:OH of from 1 to 5, preferably 1.2 to 3.

[0030] High demands are placed in particular on food packaging and on the substances used to produce said packaging. In addition to the mechanical properties, the focus is in particular on health aspects. Within the scope of the present invention, it has surprisingly been found that, by using a polyester polyol based on betulin, the formation of what are referred to as critical migratable cycles can be prevented. Critical migratable cycles are understood to mean compounds which are capable of migrating from the packaging material into the packaged product, for example an item of food, and which thus have the potential to be harmful to health. An embodiment of the adhesive composition according to the invention is therefore preferred in which the proportion of critical migratable components in the adhesive composition is less than 300 ppm, preferably less than 200 ppm, and particularly preferably less than 50 ppm, the ppm indicating the proportions by weight and the amounts relating in each case to the total weight of the solvent-free adhesive composition.

[0031] The consistency of the adhesive composition according to the invention can be adjusted according to the particular requirements, for example by adding suitable solvents. In a preferred

embodiment, the composition according to the invention further comprises one or more solvents.

[0032] Taking into account the considerable environmental and economic demands associated with the use of in particular organic solvents, it is advantageous, however, to refrain from using solvents. An embodiment is therefore preferred in which the adhesive composition according to the invention is free of solvents. It has further surprisingly been found that the use of solvents can be entirely or partly omitted when the properties of the polyester polyol used are selected appropriately. In this context, an embodiment of the adhesive composition according to the invention is therefore preferred in which the used polyester polyol based on betulin has an OH number of from 5 to 200 mg KOH/g, preferably 20 to 140 mg KOH/g. The hydroxyl number (OH number) is considered according to the invention as a measure of the number of free hydroxyl groups in a particular defined reference amount. In this case, the OH number can be determined experimentally by means of potentiometric titration or by means of acid-base titration.

[0033] The adhesive composition according to the invention can be used as a 1-component system (1K) or as a 2-component system (2K). These systems are characterized in that the adhesive is cross-linked and thus cured by means of a reaction of the NCO groups, and are also referred to as reactive adhesives.

[0034] 1K systems are characterized in that they have, as main components, polyurethane prepolymers that still have free NCO groups. In a preferred embodiment, the adhesive composition according to the invention is a 1K system in which the polyurethane prepolymers are obtained by reacting the at least one polyester polyol based on betulin with the at least one NCO-terminated compound.

[0035] 2K systems are characterized in that they comprise one component having at least one compound containing NCO groups and a second component having at least one compound that acts as a cross-linking agent and has at least two functional groups which react with NCO groups, the components being added together only immediately before application. In a preferred embodiment, the adhesive composition according to the invention is a 2K system. In a preferred embodiment, the polyester polyol based on betulin is one component and the NCO-terminated compound is the second component. In an alternatively preferred embodiment, the polyester polyol based on betulin is reacted with an isocyanate compound to form an NCO-terminated compound, which is then a first component, while a polyol compound is used as the second component.

[0036] In a preferred embodiment, the adhesive composition according to the invention is solvent-containing, solvent-free or a dispersion.

[0037] The adhesive composition according to the invention can additionally comprise further components, for example adhesion promoters. The adhesion promoter is preferably a compound which is selected from the group of alkoxysilanes. These may be organofunctional silanes such as

(meth)acryloxyfunctional, epoxy-functional, amine-functional or non-reactively substituted silanes.

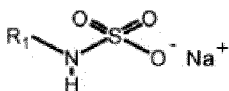
[0038] In an alternative embodiment, the adhesion promoter is preferably selected from compounds which have sulfonimide and/or amidosulfonate groups. The compounds that have sulfonimide groups are compounds that contain an $\text{SO}_2\text{-NH-C(O)}$ structure. These compounds preferably have a molecular weight below 500 g/mol, the molecular weight being calculated based on the molecular structure and it being possible to determine the molecular weight experimentally by means of mass spectrometry.

[0039] In a preferred embodiment, the adhesion promoter having a sulfonimide structure or amidosulfonate structure is one or more of the following compounds I to VI.

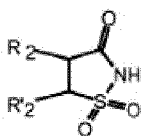
I) $\text{R}_1\text{-NH-SO}_3\text{H}$ and salts thereof where $\text{R}_1 = \text{C}_n\text{H}_{2n+1}$ where $n = 1$ to 10, cyclohexyl, phenyl, alkyl-substituted cyclohexyl or phenyl;

II) $\text{R}'_4\text{-SO}_2\text{-NH-C(O)-R}_4$ where $\text{R}_4, \text{R}'_4 = \text{C}_n\text{H}_{2n+1}$ where $n = 1$ to 10, cyclohexyl, phenyl, alkyl-substituted cyclohexyl or phenyl; or where R_4 and R'_4 are of the kind that form a common, optionally alkyl-substituted C_2 or C_3 bridge as a component of an aliphatic or aromatic 5- or 6-membered ring, where R_4 and R'_4 are the same or different;

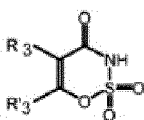
III) $\text{R}'_5\text{-O-SO}_2\text{-NH-C(O)-R}_5$ where $\text{R}_5, \text{R}'_5 = \text{C}_n\text{H}_{2n+1}$ where $n = 1$ to 10, cyclohexyl, phenyl, alkyl-substituted cyclohexyl or phenyl; or where R_4 and R'_4 are of the kind that form a common, optionally alkyl-substituted C_2 or C_3 bridge as a component of an aliphatic or aromatic 5- or 6-membered ring, where R_5 and R'_5 are the same or different;



IV) where R_1 is defined as in I).



V) where $\text{R}_2, \text{R}'_2 = \text{C}_n\text{H}_{2n+1}$ where $n = 1$ to 10, cyclohexyl, phenyl, alkyl-substituted cyclohexyl or phenyl; or where R_2 and R'_2 are of the kind that form a common, optionally alkyl-substituted C_2 or C_3 bridge as a component of an aliphatic or aromatic 5- or 6-membered ring, where R_2 and R'_2 are the same or different;



VI) where $\text{R}_3, \text{R}'_3 = \text{C}_n\text{H}_{2n+1}$ where $n = 1$ to 10, cyclohexyl, phenyl, alkyl-substituted cyclohexyl or phenyl; or where R_3 and R'_3 are of the kind that form a common, optionally alkyl-

substituted C₂ or C₃ bridge as a component of an aliphatic or aromatic 5- or 6-membered ring, where R₃ and R'₃ are the same or different.

[0040] In particular, substituted amidosulfonates, such as cyclohexylamidosulfonate, substituted or unsubstituted benzene sulfimides (benzoic acid sulfimides) such as 1,2-benzisothiazole-3(2H)-one-1,1-dioxide, or alkyl-substituted 3,4-dihydro-1,2,3-oxathiazine-4-one-2,2-dioxides (1,2,3-oxathiazine-4(3H)-one-2,2-dioxides) such as 6-methyl-3,4-dihydro-1,2,3-oxathiazine-4-one-2,2-dioxide, are used as the adhesion promoter in the adhesive composition according to the invention.

[0041] Mixtures of the above-mentioned compounds can also be used as the adhesion promoter.

[0042] In a preferred embodiment, the adhesive composition according to the invention can contain additional components and additives. These additional components and additives are preferably plasticizers, catalysts, resins, stabilizers, pigments and/or fillers.

[0043] The catalyst is preferably a metal compound of Sn, Ti, Fe, Zn, Bi, Hg, Pb, or tertiary amines.

[0044] The catalyst is particularly preferably titanates such as tetrabutyl titanate and tetrapropyl titanate, tin carboxylates such as dibutyltin dilaurate (DBTL), dibutyltin diacetate, tin octoate, tin oxides such as dibutyltin oxide and dioctyltin oxide, organoaluminum compounds such as aluminum trisacetalacetate, aluminum trisethylacetate, chelate compounds such as titanium tetraacetylacetate, amine compounds such as triethylenediamine, guanidine, diphenylguanidine, 2,4,6-tris(dimethylaminomethyl)phenol, morpholine, N-methylmorpholine, 2-ethyl-4-methylimidazole, 1,8-diazabicyclo-(5,4,0)-undecane-7 (DBU), 1,4-diazabicyclooctane (DABCO), 1,4-diazabicyclo[2,2,2]octane, N,N-dimethylpiperazine, 1,8-diazabicyclo[5,4,0]undec-7-ene, dimorpholinodimethylether, dimorpholinodiethylether (DMDEE) and mixtures thereof.

[0045] In this case, the amount of catalysts is preferably 0.01 to 5 wt.%, particularly preferably 0.05 to 2 wt.%, based on the total weight of the solvent-free adhesive composition.

[0046] In the food packaging industry, film-like substrates are predominantly used, such as metal foils or plastics films. Adhesives used in this composition are referred to as lamination or laminating adhesives. In a preferred embodiment, the adhesive composition according to the invention is a laminating adhesive composition. In a further preferred embodiment, the adhesive composition according to the invention is a lamination adhesive composition.

[0047] The present invention further relates to a method for preparing the adhesive composition according to the invention. The method according to the invention comprises the following steps:

- a) providing a mixture comprising betulin and at least one triglyceride;
- b) reacting the reaction product obtained from the mixture in step a) with an NCO-terminated compound.

[0048] In a preferred embodiment, the product obtained by the reaction in step b) is, in an additional step, reacted with another polyol component in order to obtain the adhesive composition according to the invention.

[0049] The present invention further relates to an adhesive that can be obtained by curing the adhesive composition according to the invention. It has surprisingly been found that the combination of the components of the adhesive composition according to the invention allows energy-efficient curing at low temperatures. An embodiment is therefore preferred in which the adhesive composition according to the invention is cured at less than 80 °C, preferably less than 60 °C, particularly preferably less than 40 °C and in particular at room temperature.

[0050] The adhesive according to the invention is suitable in particular for bonding film-like substrates. A parameter that is of significance for such an application is the adhesion that the bonded material and thus the adhesive has. In a preferred embodiment, the adhesive according to the invention has an adhesion of more than 2.0 N/15 mm, preferably more than 3.0 N/15 mm, the adhesion having been determined in accordance with DIN 53357. It has surprisingly been found that these values can also be achieved under stress, for instance after sterilization and bag sterilization. In this case, the sterilization can be carried out by means of UV radiation, heat or steam, for example. It has surprisingly been found that the adhesion can also be achieved in the case of aggressive filling materials, for example ingredients containing oleic acid.

[0051] The adhesive composition according to the invention and the adhesive according to the invention are suitable in particular for bonding film-like substrates, in particular for producing food packaging. The present invention therefore further relates to the use of the adhesive composition according to the invention and/or the adhesive according to the invention as a laminating and/or lamination adhesive. In a preferred embodiment, the adhesive composition according to the invention and/or the adhesive according to the invention is used to bond film-like substrates.

[0052] The present invention further relates to a method for bonding at least two substrates, wherein the adhesive composition according to the invention is applied to at least one substrate and the at least two substrates are subsequently joined together. In a preferred embodiment, at least one of the substrates has a metal surface or a printed surface. In another preferred embodiment, the at least two substrates are film-like substrates, preferably metal foils and/or plastics films.

[0053] Flexible films are preferably used as film materials in the method according to the invention. In addition to metal foils, for example aluminum foils, examples of said flexible films are thermoplastic plastics materials in film form, such as polyolefins, polyethylene (PE) or polypropylene (PP, CPP, OPP), polyvinyl chloride (PVC), polystyrene (PS), polyesters such as PET, polyamide, natural polymers such as cellophane or paper. The film materials used can be surface-modified before use, for example by modifying the polymers with functional groups or by means of corona or plasma treatment or flame-scarfing. Additional components, for example pigments and dyes may further be

contained. The film material may additionally comprise foamed layers.

[0054] In a preferred embodiment, the amount of adhesive applied is 1 to 100 g/m², preferably 2 to 70 g/m².

[0055] In a preferred embodiment, the substrates can optionally be subjected to a pretreatment and/or the two substrates are joined together under pressure.

[0056] The present invention further relates to an article which comprises the adhesive composition according to the invention or the adhesive according to the invention. In a preferred embodiment, the article can be obtained in accordance with the method according to the invention. The article is preferably a multi-layered substrate, in particular for packaging for food and pharmaceutical products.

[0057] The present invention will be explained in more detail with reference to the following examples, said examples not being intended to be considered to limit the inventive concept.

Examples:

[0058] Table 1 shows the monomer composition of a polyester polyol as used in the adhesive composition according to the invention, the weight amounts being given in grams in each case. The information in brackets gives the proportions in mol.%.

Table 1:

Monomer	Example 1	Example 2
Betulin	64.78 g (30.5 mol.%)	75.78 g (17.8 mol.%)
Castor oil	135.16 g (30.5 mol.%)	379.40 g (42.7 mol.%)
Succinic acid	22.08 g (39 mol.%)	44.85 g (39.5 mol.%)

[0059] Table 2 summarizes selected properties of the polyester polyol.

Table 2:

	Viscosity (140 °C)	T _g *	Polydispersity	OH number	M _n
Example 1	180 mPas	-35 °C	2.3	71 mg KOH/g	2508 g/mol
Example 2	100 mPas	-51 °C	2.5	70 mg KOH/g	2984 g/mol

*T_g = glass transition temperature (DSC)

[0060] From the molar mass distribution curve, which was determined using GPC, the relative

number-average and weight-average molar mass average values were calculated, and the polydispersity was determined therefrom.

[0061] The polyesters each have an acid number of 1.8 mg KOH/g sample.

[0062] The polyesters were tested for migratable cycles. For this purpose, diisocyanate 4,4'-MDI (NCO/OH 1.43) was added to samples, and said samples were mixed and poured out onto teflon paper. The reaction mixture was cured for 14 days at ambient atmosphere. The films obtained were further processed and analyzed using GC-MS as follows.

[0063] The adducts obtained and a reference were weighed in headspace vials and mixed with 99.8% ethanol. The containers were then tightly sealed and the samples were extracted for two hours at 70 °C. 1 ml was then taken from each of the extracts, mixed with an internal standard (naphthalene-D8) and measured using GC-MS. 1 g substance was extracted per sample. The identification was carried out using manual spectra interpretation. The qualification was carried out with respect to naphthalene-D8 with a resonance factor 1 (RF = 1). No critical cyclic compounds could be detected.

[0064] The polyesters were reacted with an NCO-terminated compound, a ratio of NCO/OH of 2.32 being selected. As the NCO-terminated compound, the commercially available NCO-component Loctite Liofol LA 7371 was used, as well as a mixture of pentamethylene diisocyanate trimer (PDI trimer), 1-isocyanatomethyl-3-isocyanato-1,5,5-trimethylcyclohexane (IPDI) and aminosilane, referred to in the table as PDI trimer.

[0065] The mechanical properties of the adhesives were tested as follows:

[0066] The substrates to be coated (PET/aluminum preliminary bond and polypropylene (PP)) were formatted to DIN A4 size. The carrier film PET/Al was then fixed to a planar surface and the adhesive composition was applied to the aluminum side of the pre-composite by means of a doctor blade. The coated carrier film was subsequently dried in a drying cabinet at 90°C for 5 minutes.

[0067] The composites thus obtained were cured under pressure (8 kg) between metal plates in a drying cabinet at room temperature or 40 to 60 °C. The adhesion of the laminate was checked after 7 and after 14 days. In addition, the adhesion was measured after sterilization and bag sterilization using an aggressive filling material (consisting of 0.1% oleic acid, water and corn starch). The determined values are summarized in Table 3.

[0068] The commercially available adhesive Loctite Liofol LA 2760 / LA 7371 was used as a comparison.

Table 3:

Adhesive		ADH ₁₄ ¹⁾		ADH _{st} ²⁾		ADH _{bag} ³⁾	
Polyesterpolyol	NCO	Value	Appearance	Value	Appearance	Value	Appearance
Example 1	PDI	4.3	sep	7.7	MS ⁴⁾	5.9	MS
	trimer	4.6	sep	7.6	MS	5.8	MS
Example 1	Loctite	4.5	sep	6.7	MS	5.4	MS
	LA 7371	5.8	MS	6.9	MS	5.8	MS
Example 2	PDI	2.4	sep	4.5	sep ⁵⁾	2.7	sep
	trimer	1.8	sep	4.4	sep	2.5	sep
Example 2	Loctite	3.1	sep	3.8	sep	2.3	sep
	LA 7371	2.2	sep	4.4	sep	3.1	sep
Comparison	Loctite LA 7371	2.4	sep	5.3	sep	0.0	delam ⁶⁾

¹⁾ adhesion after 14 days

²⁾ adhesion after sterilization (131 °C/45 min) 14 days

³⁾ adhesion after bag sterilization (131 °C/30 min) 14 days; corn starch/oleic acid (0.1%)

⁴⁾ MS: material strain

⁵⁾ sep: separation

⁶⁾ delam: delamination

[0069] As can be seen in Table 3, using the adhesive according to the invention good levels of adhesion were achieved which could not be achieved using conventional polyester-polyol-based adhesives.

Claims:

1. An adhesive composition comprising:
 - a) at least one polyester polyol based on betulin; and
 - b) at least one NCO-terminated compound.
2. The adhesive composition according to claim 1, characterized in that the polyester polyol based on betulin is obtained by reacting betulin and one or more triglycerides.
3. The adhesive composition according to one or more of the preceding claims, characterized in that the polyester polyol is obtained from a reaction mixture that comprises the following monomer units:
 - i) betulin in an amount of from 5 to 50 wt.%, preferably 25 to 35 wt.%;
 - ii) dicarboxylic acid in an amount of from 5 to 45 wt.%, preferably 8 to 40 wt.%; and
 - iii) triglyceride in an amount of from 20 to 80 wt.%, preferably 40 to 70 wt.%,in each case based on the total weight of the monomer units.
4. The adhesive composition according to one or more of the preceding claims, characterized in that the dicarboxylic acid is selected from the group consisting of succinic acid, adipic acid, azelaic acid, sebacic acid, dodecanoic acid, tetradecandioic acid, furandicarboxylic acid, isophthalic acid, terephthalic acid, orthophthalic acid and mixtures thereof.
5. The adhesive composition according to claim 3, characterized in that the triglyceride is selected from the group consisting of soybean oil, linseed oil, sunflower oil, safflower oil, rapeseed oil, physic nut oil, light walnut oil, grapeseed oil, canola oil, corn oil, cashew kernel oil, fish oil, castor oil, tall oil, coconut oil, palm oil, palm kernel oil, olive oil and mixtures thereof and derivatives thereof as well as synthetic or biotechnologically prepared triglycerides.
6. The adhesive composition according to one or more of the preceding claims, characterized in that the NCO-terminated compound is selected from the group consisting of 1,5-naphthylene diisocyanate (NDI), 2,4'- or 4,4'-diphenylmethane diisocyanate (MDI), isomers of toluene diisocyanate (TDI), methylene triphenyl triisocyanate (MIT), hydrogenated MDI (H12MDI), tetramethylxylene diisocyanate (TMXDI), 1-isocyanatomethyl-3-isocyanato-1,5,5-trimethylcyclohexane (IPDI), xylene diisocyanate (XDI), hexane-1,6-diisocyanate (HDI), pentamethylene diisocyanate (PDI), dicyclohexylmethane diisocyanate and mixtures thereof.

7. The adhesive composition according to one or more of the preceding claims, characterized in that the proportion of polyester polyol based on betulin is 20 to 90 wt.%, preferably 30 to 80 wt.%, particularly preferably 40 to 60 wt.%, in each case based on the total weight of the solvent-free adhesive composition.
8. The adhesive composition according to one or more of the preceding claims, characterized in that the proportion of NCO-terminated compound is 10 to 80 wt.%, preferably 20 to 70 wt.%, particularly preferably 30 to 60 wt.%, in each case based on the total weight of the solvent-free adhesive composition.
9. The adhesive composition according to one or more of the preceding claims, characterized in that the composition has a ratio of NCO:OH of from 1 to 5, preferably 1.2 to 3.
10. The adhesive composition according to one or more of the preceding claims, characterized in that the proportion of critical migratable components in the composition is less than 300 ppm, preferably less than 200 ppm, particularly preferably less than 50 ppm, in each case based on the total weight of the solvent-free adhesive composition.
11. A method for preparing an adhesive composition according to one or more of claims 1 to 10, comprising the following steps:
 - a) providing a mixture comprising betulin and at least one triglyceride;
 - b) reacting the reaction product obtained from the mixture in step a) with an NCO-terminated compound.
12. An adhesive obtainable by curing an adhesive composition according to one or more of claims 1 to 10.
13. The use of an adhesive composition according to one or more of claims 1 to 10 or an adhesive according to claim 12 as a laminating adhesive.
14. An article comprising an adhesive composition according to one or more of claims 1 to 10 or an adhesive according to claim 12.
15. A method for bonding at least two substrates, characterized in that an adhesive composition according to one or more of claims 1 to 10 is applied to at least one substrate and the at least two substrates are subsequently joined together.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/065968

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09J175/14 C09J175/06 C08G18/42 C08G18/68 C08G18/73
C08G18/75 C08G18/72 C08G18/79 B32B27/40

ADD.

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)

C09J C08G B32B

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2018/095962 A1 (HENKEL AG & CO KGAA [DE]) 31 May 2018 (2018-05-31) page 16; example 1 claims 8-12	1-15
A	----- ERA V ET AL: "FATTY ACID ESTERS FROM BETULINOL", JOURNAL OF THE AMERICAN OIL CHEMISTS' SOCIETY (JA, SPRINGER, DE, vol. 1, 1 January 1981 (1981-01-01), pages 20-23, XP008075263, ISSN: 0003-021X rechte Spalte, Absatz: "Preparation of Coatings"; page 22 ----- -/-	1-15



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

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"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

2 September 2019

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19/09/2019

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/065968

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Jekaterina Jeromenok: "Polymers from the Natural Product Betulin; A Microstructural Investigation", 12 March 2012 (2012-03-12), XP055533576, Germany DOI: 10.1002/marc.201600748 Retrieved from the Internet: URL:https://d-nb.info/1025584961/34 [retrieved on 2018-12-12] Absatz 4.3.1; page 70 - page 78 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/065968

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		KR 20190086515 A	22-07-2019
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