(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 January 2018 (11.01.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/007548 A1

(51) International Patent Classification:
C09J 129/04 (2006.01) *C09J 133/08* (2006.01)

(21) International Application Number:
PCT/EP2017/066990

(22) International Filing Date:
06 July 2017 (06.07.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
16382323.0 07 July 2016 (07.07.2016) EP

(71) Applicant: **REPSOL, S.A.** [ES/ES]; C/ Méndez Álvaro,44, 28045 Madrid (ES).

(72) Inventors: **MARÍN PERALES, Laura**; Centro de Tecnología de Repsol, Ctra. De Extremadura, A-5, km, 28935 Móstoles, Madrid (ES). **RODRÍGUEZ BUEY, María Luisa**; Centro de Tecnología de Repsol, Ctra. De Extremadura, A-5, km, 28935 Móstoles, Madrid (ES). **POLO ABAD, Rafael**; Centro de Tecnología de Repsol, Ctra. De Extremadura, A-5, km, 28935 Móstoles, Madrid (ES). **REAL GUERRERO, Ana Isabel**; Centro de Tecnología de Repsol, Ctra. De Extremadura, A-5, km, 28935 Móstoles, Madrid (ES). **GARCÍA RUIZ, Mónica**; Centro de Tecnología de Repsol, Ctra. De Extremadura, A-5, km, 28935 Móstoles, Madrid (ES). **MÉNDEZ LLATAS, Luis Miguel**; Centro de Tecnología de Repsol, Ctra. De Extremadura, A-5, km, 28935 Móstoles, Madrid (ES). **MARTÍN MARTÍNEZ, José Miguel**; Universidad de Alicante, Carretera San Vicente del Raspeig, s/n, 03690 San Vicente del Raspeig, Alicante (ES). **LLORENS ESTEVE, Juan**; Universidad de Alicante, Carretera San Vicente del Raspeig, s/n, 03690 San Vicente del Raspeig, Alicante (ES). **YÁÑEZ PACIOS, Andrés Jesús**; Universidad de Alicante, Carretera San Vicente del Raspeig, s/n, 03690 San Vicente del Raspeig, Alicante (ES).

(74) Agent: **BALDER IP LAW, S.L.**; Paseo de la Castellana 93, 5ª planta, 28046 Madrid (ES).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

WO 2018/007548 A1

(54) Title: COMPOSITIONS OF POLYHYDROXYALKANOATES AND POLAR POLYMERS

(57) Abstract: The present invention is directed to a polymer composition comprising a medium chain length polyhydroxyalkanoate (mcl-PHA) and a polar polymer (e.g. co-polymers of ethylene and vinyl acetate). The invention further includes adhesives based on the composition and manufacturing methods thereof.

COMPOSITIONS OF POLYHYDROXYALKANOATES AND POLAR POLYMERS

FIELD OF THE INVENTION

The invention relates to biodegradable compositions of polar polymers containing polyhydroxyalkanoates, which provide improved pressure sensitive adhesives (PSA), hot melt adhesives and hot melt PSA compositions (HMPSA).

BACKGROUND OF THE INVENTION

The chemical industry is continuously searching for new polymers and polymer compositions with improved properties. The field of adhesives is not an exception, and important efforts to develop new products with improved properties are currently carried out. The interest is not limited to moderate the adhesion, but to improve the rheological properties, the stability or reducing their environmental impact.

WO 2004/076582 discloses a mixture of two polyhydroxyalkanoates (PHAs). Although no examples are given, it is generically indicated that one of the polymers can be 3-hydroxydodecanoate or 3-hydroxydodecenoate. Different mixtures are tested, all including polyhydroxybutyrate (PHB) in their structure. No mention of mixtures of PHAs with polar polymers is provided.

WO 2004/076583 A1 discloses a "moderately strong bond" for R-3-hydroxyoctanoate when applied between two Mylar polyester films. This document generically mentions the possibility of using additives, but does not provide any example or evidence. Examples 10-12 of D2 use polyhydroxyoctane neat, without mixing at all with other components.

WO 96/05264 A1 discloses adhesive compositions comprising PHAs, for example, polyhydroxyoctanoate or polyhydroxynonanoate. The compositions of D3 include a tackifier and have good tack properties, but do not disclose or suggests the possibility of mixing a PHA with polar polymer.

WO 02/10303 A2 discloses adhesive compositions comprising polycaprolactone and a tackifying agent specifically selected for compatibility thereof.

WO 2002/34857 discloses (met)acrylate-modified PHA in order to produce crosslinking, but no mixtures of PHAs with polar polymers or ethylene copolymers. The polymers disclosed in WO 2002/34857 have a number average molecular weight that is under about 50,000 Da, typically from

about 500 to about 8,000 Da are described.

WO 1995/02649 mentions the use of PHA (short chain, e.g. polyhydroxybutyrate (PHB) or poly 3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV)) as an adhesive between layers; however, poor adhesion at low temperature is shown.

WO 2004/101683 describes mixtures of PHAs and other polymers. The PHAs can be co-polymers of a first hydroxyl ester C_3-C_6 monomer (formula I) and a second hydroxyl ester C_6-C_{22} monomer (formula (II)). No adhesive compositions are discussed. On the contrary, stickiness is seen as a negative feature of the polymer (last paragraph of page 1).

WO 2013/162059 discloses a mixture of short chain PHA (e.g. PHB or PHBV) and a "polar functional group modified polyolefin based polymer". The application provides specific examples for ethylene/methyl acrylate/glycidyl methacrylate copolymerized resin, although never in combination with PHA.

WO 2016/166292, claiming priority of April 17, 2015, and published October 20, 2016, refers to mixtures of mcl-PHAs with poly(alkylene carbonates).

US 5,169,889 discloses an adhesive blend comprising PHBV or PHB with an EVA polymer, including examples M and N (table 6) showing hot melt compositions comprising Biopol (PHBV) and 10% of Elvax 40 or Vinathene 90500 (EVA polymers, 40% and 50% vinyl content, respectively).

SUMMARY OF THE INVENTION

The present invention provides compositions of PHAs and polar polymers with improved properties. Thus, a first embodiment of the invention is a composition, preferably an adhesive composition, comprising

(i) a polyhydroxyalkanoate wherein one of the monomers of said polyhydroxylalkanoate comprises 7 or more carbon atoms, and all monomers of said polyhydroxylalkanoate comprise 6 or more carbon atoms;

(ii) more than 10 wt% with respect to the total weight of the composition of at least one polar polymer; and

(iii) optionally further components to complete the 100 wt% of the composition.

Thus, component (i) includes medium-chain length polyhydroxyalkanoates and long-chain length

polyhydroxyalkanoates. Said component (i) is also referred to as "mcl-PHA" in the present disclosure.

The compositions of the invention solve several problems of the current adhesives. Firstly, the mcl-PHA is a polymer of natural origin which can substitute some components of the hot melt and PSA (pressure sensitive adhesives). It is has been found that mcl-PHAs are surprisingly suited to replace other components of synthetic origin or which, being of natural origin, require further modifications in order to be used. Even further, the compositions of the invention do not require the use of cross-linkers in order to provide for sufficient cohesive strength. Thus, it is an embodiment of the invention to provide a composition comprising no crosslinkers. It is thus preferable that they are thermoplastic polar polymers. The compositions of the invention therefore reduce their carbon footprint. Even more surprisingly is the finding that the compositions of the invention display improved tackiness and peel strength at very low temperatures. This could not been foreseen even by previous studies of adhesives including short chain PHAs (e.g. example M and N in the US 5,169,889).

Thus, the compositions of the invention can be made into hot melt, PSA or HMPSA adhesives.

The present invention opens the door to a new family of biodegradable adhesive compositions having low temperature tackiness, peel strength and adhesion.

Further aspects of the invention are accordingly pressure sensitive adhesives (PSA), hot melt adhesives or hot melt PSA compositions (HMPSA) comprising the compositions of the invention.

A further aspect of the invention is the use of a polyhydroxyalkanoate as a tackifier in an adhesive composition wherein one of the monomers of said polyhydroxylalkanoate comprises 7 or more carbon atoms, and all monomers of said polyhydroxylalkanoate comprise 6 or more carbon atoms.

A further aspect of the invention is a method for the preparation of the compositions of the invention which comprises mixing of the polar polymer and the mcl-PHA at temperature which is sufficient to melt both components.

DESCRIPTION OF THE INVENTION

Polar Polymers

Polar polymers according to the present invention are considered those polymers which comprise carbon-heteroatom bonds, except poly(alkylene carbonates). Polar polymers are typically considered those comprising at least a 5 molar % of carbon-heteroatom bonds (C-Het%), preferably 10 molar % of

carbon-heteroatom bonds (C-Het%), preferably comprising at least 15 molar % of carbon-heteroatom bonds, more preferably at least 20 molar % of carbon-heteroatom bonds, with respect to the sum of carbon-carbon bonds and carbon-heteroatom bonds, except poly(alkylene carbonates). The molar % of carbon-heteroatom bonds (C-Het%) is measured by counting in the monomer unit the number of carbon-heteroatom bonds versus the sum of carbon-heteroatom bonds and carbon-carbon bonds, according to the following formula C-Het (%)= 100 x [C-Het/(C-Het + C-C)]. Double and triple bonds count one. For example, for a (meth)acrylate acid the monomeric unit is (-CH_2-C(CH_3)(C(=O)OH)-). The number of carbon-carbon bonds is 4, and the number of carbon-heteroatom bonds is 2. C-Het% is in this case 100 x (2/(4+2)= 33.3%.

The compositions of the invention comprise typically polar polymers used in adhesive compositions, such as PSA, hot melt adhesive or HMPSA compositions. These polymers frequently used in the adhesive industry, are understood in the polymer field as polymers comprising polar groups, such as, for example, those consisting of the group selected from hydroxyl (C-OH), ketone (C(=O)), aldehyde (C(=O)H), ester (C(=O)-O-C), acid (C(=O)OH), ether (C-O-C), amine (C-NH_2 or C-N(H)-C or C-N(C)-C) or , amide (C(=O)NH_2 or C(=O)N(H)-C or C(=O)N(C)-C), nitrile (C-CN), urea(C-N-C(=O)-N), isocyanate (C-NCO), thiol (C-SH) and mixtures thereof, but not including carbonates. For example, typical polar polymers used in hot melt, PSA or HMPSA adhesives are copolymers of unsaturated hydrocarbon and an acrylate ester or acid, or copolymers of an unsaturated hydrocarbon and a vinyl saturated aliphatic ester or polyvinylalcohol (PVOH) or polyamides or polyesters or polyurethanes or vinyl ethers or polyolefins grafted with polar groups or mixtures thereof. The unsaturated hydrocarbon monomer usually comprises a short chain, typically, ethylene, propylene or butylene, but unsaturated hydrocarbons with more carbons are possible. The most frequently used is ethylene.

Examples of copolymers of unsaturated hydrocarbon and a acrylate ester or acid available to the skilled person are copolymers of unsaturated hydrocarbons and acrylic acid or esters of (meth)acrylate (C_1-C_{22} alkyl esters, e.g. methylmethacrylate) or acrylonitrile. Said acrylate ester or acid may have the following formula CH_2=C(R_1)C(=O)OR_2, wherein R_1 is hydrogen or a C_1-C_4 aliphatic saturated hydrocarbon, and R_2 is hydrogen of a C_1-C_8 aliphatic saturated hydrocarbon. Some exemplary acrylate esters or acids are methyl (meth)acrylate, ethyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, hexyl (meth)acrylate, 2-ethylbenzyl acrylate, lauryl acrylate, cetyl acrylate, stearyl acrylate, eicosyl acrylate, isodecyl acrylate, dodecyl (meth)acrylate, hydroxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, butyl (meth)acrylate or Trimethylolpropane triacrylate (TMPTA), benzyl acrylate, cyanoethyl acrylate, 2,2,2-trifluoroethyl (meth)acrylate. Exemplary polymers of this class are thus ethylene methyl acrylate

(EMA), ethylene methyl methacrylate (EMMA), ethylene butyl acrylate (EBA), ethylene acrylic acid (EEA). Examples of copolymers of an unsaturated hydrocarbon and a vinyl saturated aliphatic ester typically comprise a vinyl C_1-C_4 saturated aliphatic ester. The most frequently used copolymer of an unsaturated hydrocarbon and a vinyl saturated aliphatic ester is ethylene-vinyl acetate (EVA) and ethylene n-butyl acrylate (EBA).

Polyamides are polymers having repeating units linked by an amide bond, typically an aliphatic or aromatic repeating unit. Examples of polyamides are nylons.

Another further class of polar polymers that can be used in the compositions of the invention is polyurethanes, preferably thermoplastic polyurethanes (TPUs). TPUs are block copolymers formed by reacting diisocyanates, short-chain diols (chain extenders) and long-chain polyols. Many different types exist depending on the specific composition and functionality of each of the three components. Thus, for example, the TPU is preferably based on a polyol (long-chain diol), an aliphatic diisocyanate and a chain extender. Many TPUs are available in the market from different vendors, such as, for example, Irogran™ (Huntsman), Estane™ (Lubrizol), Desmocoll™ or Elasthane™ (DSM).

The polar polymer is typically selected from the group of copolymers of ethylene and vinyl acetate, copolymers of ethylene and a (met)acrylate, a thermoplastic polyurethane, PVOH and mixtures thereof.

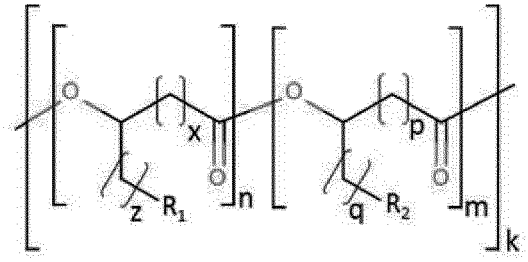
The compositions of the invention are especially suited for PSA and HMPSA compositions, especially PSA compositions, which typically reduce their tack at low temperatures. Surprisingly, the PSAs based on the composition of the invention show excellent tack at low temperatures.

medium-chain length Polyhydroxyalkanoates (mcl-PHAs)

PHB or PHBHV have been used in adhesive mixtures in the past (US 5,169,889). The inventors have discovered that mcl-PHAs provide improved adhesive compositions when mixed with polar polymers.

mcl-PHAs are typically synthesized by a broad range of natural and genetically engineered bacteria as well as genetically engineered plant crops (Braunegg et al., 1998, J. Biotechnology 65: 127-161; Madison and Huisman, 1999, Microbiology and Molecular Biology Reviews, 63: 21-53; Poirier, 2002, Progress in Lipid Research 41: 131-155). Useful microbial strains for producing mcl-PHAs, include, but are not limited to *Alcaligenes eutrophus* (renamed as *Ralstonia eutropha*), *Alcaligenes latus*, *Azotobacter*, *Aeromonas*, *Comamonas*, *Pseudomonas*, and genetically engineered organisms including genetically engineered microbes such as *Pseudomonas, Ralstonia* and *Escherichia coli*.

For example, the mcl-PHA used in the composition of the invention comprises one or more mcl-PHA, wherein each one is independently chosen from a mcl-PHA of formula (II) and stereoisomers thereof



(II)

wherein

n, m or k are each independently an integer;

p and q are integers adding in each case between 3 and 40;

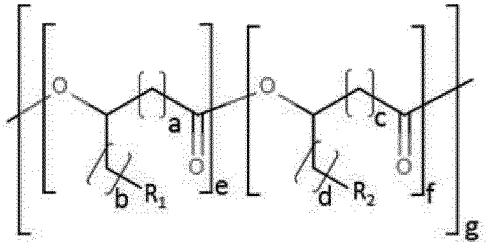
x and z are integers adding in each case between 4 and 40; and

each of R_1 and R_2 is methyl.

The mcl-PHA of the invention can be a mixture of 2, 3, 4, 5, 6, 7, 8 or 9 mcl-PHAs, or even more. Even further, the mcl-PHA can be a mixture of polymers, each incorporating 2 or more, for example, 2, 3, 4, 5, 6, 7, 8 or 9, or more, monomers, wherein at least one of the monomers comprises 7 or more carbon atoms, and all monomers comprise 6 or more carbon atoms. Each mcl-PHA is typically one that comprises beta-substituted monomers, wherein x or p are 1, preferably wherein x and p are 1. One or more mcl-PHAs may however comprise a gamma-substituted monomer wherein x or p are 2. p and q can be integers adding in each case between 3 and 40, and x and z are integers adding in each case between 5 and 40. p and q can also be integers adding in each case between 4 and 40, and x and z are integers adding in each case between 4 and 20. Even further, p and q can be integers adding in each case between 3 and 18; and x and z are integers adding in each case between 5 and 16. Also, x can be 1 for every n or m and z can be in each case selected from the group consisting of 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24 and 25, preferably in each case selected from the group consisting of 8, 9, 10, 11, 12, 13, 14, 15, 16, 17 and 18. According to another example, x and p are 1 for every n and m, and each of p and z is independently selected from the group consisting of 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24 and 25. The integers n, m and k determine the size and molecular weight of the mcl-PHA and their value is not critical for the present invention, and can each independently be comprised between 1 and 10,000 as long as k is at least 1 and the sum of n and m is at least 1 (e.g. 10-8,000), typically between 25 and 1,000, for example

between 30 and 900 or between 50 and 800, more typically between 100 and 700.

The mcl-PHA used in the composition of the invention can be one of formula (III), which includes stereoisomers thereof



(III)

wherein e, f or g are each independently and integer;

c is in each case 1, 2 or 3;

a is in each case 1, 2 or 3;

b and d are in each case integers independently selected from 3 to 24; and

each of R_1 and R_2 is independently methyl.

For example, the mcl-PHA comprises two alpha-substituted monomers, i.e. a mcl-PHA wherein a and c are both 1.

The mcl-PHA used in the invention is preferable a mixture of different mcl-PHAs. Thus, in the present disclosure, it can be understood that "said polyhydroxyalkanoate" or "a polyhydroxyalkanoate" or "one polyhydroxyalkanoate" or the similar terms, refer to a mixture of mcl-PHAs wherein at least one, preferably all of them, comprise one monomer having 7 or more carbon atoms, and all monomers comprise 6 or more carbon atoms. It is preferred that the said mcl-PHA polymer mixture comprises between 2 and 15, preferably between 3 and 12 different monomers wherein one of the monomers comprises 7 or more carbon atoms, and all monomers of said comprise 6 or more carbon atoms. Many different combinations are possible within the inventive concept of the present disclosure, and only a few are listed below as non-limiting possibilities.

An example of such mcl-PHA polymer mixture comprises between 0.1 wt% and 99 wt% of 3-hydroxyhexanoate, and between 0.1 wt% and 99 wt% of 3-hydroxyoctanoate.

A further example of such mcl-PHA polymer mixture comprises between 0.1 wt% and 99 wt% of 3-hydroxyhexanoate, and between 0.1 wt% and 99 wt% of 3-hydroxydodecanoate.

A further example of such mcl-PHA polymer mixture comprises between 0.1 wt% and 99 wt% of 3-hydroxyhexanoate, and between 0.1 wt% and 99 wt% of 3-hydroxytetradecanoate.

Many other combinations are also possible, for example between 0.1 wt% and 50 wt% of 3-hydroxyhexanoate, between 0.1 wt% and 50 wt% of 3-hydroxyoctanoate, between 0.1 wt% and 50 wt% of 3-hydroxydecanoate, between 0.1 wt% and 50 wt% of 3-hydroxydodecanoate, between 0.1 wt% and 50 wt% of 3-hydroxytetradecanoate and between 0.1 wt% and 50 wt% of 3-hydroxyhexadecanoate.

Another possible mixture is a for example between 1 wt% and 10 wt% of 3-hydroxyhexanoate, between 10 wt% and 50 wt% of 3-hydroxyoctanoate, between 10 wt% and 50 wt% of 3-hydroxydecanoate, between 5 wt% and 30 wt% of 3-hydroxydodecanoate, between 0.5 wt% and 20 wt% of 3-hydroxytetradecanoate and between 0.1 wt% and 20 wt% of 3-hydroxyhexadecanoate.

A further example of such mcl-PHA polymer mixture comprises between 0 wt% and 99 wt% of 3-hydroxyhexanoate, and at least one of between 0.1 wt% and 99 wt% of 3-hydroxyoctanoate, between 0.1 wt% and 99 wt% of 3-hydroxydecanoate, between 0.1 wt% and 99 wt% of 3-hydroxydodecanoate, between 0.1 wt% and 99 wt% of 3-hydroxytetradecanoate, between 0.1 wt% and 99 wt% of 3-hydroxyhexadecanoate, between 0.1 wt% and 99 wt% of 3-hydroxyoctadecanoate, between 0.1 wt% and 99 wt% of 3-hydroxyicosanoate, between 0.1 wt% and 99 wt% of 3-hydroxydocosanoate, between 0.1 wt% and 99 wt% of hydroxytetracosanoate, between 0.1 wt% and 99 wt% of 3-hydroxyhexacosanoate.

A further example of such mcl-PHA polymer mixture comprising monomer units including carbon-carbon double bonds, comprises between 0.1 wt% and 99 wt% of 3-hydroxyhexanoate, and at least one of between 0.1 wt% and 99 wt% of 3-hydroxyoctanoate, between 0.1 wt% and 99 wt% of 3-hydroxydecanoate, between 0.1 wt% and 99 wt% of 3-hydroxydodecanoate, between 0.1 wt% and 99 wt% of 3-hydroxydodecenoate, between 0.1 wt% and 99 wt% of 3-hydroxytetradecanoate, between 0.1 wt% and 99 wt% of 3-hydroxytetradecenoate, between 0.1 wt% and 99 wt% of 3-hydroxyhexadecanoate, between 0.1 wt% and 99 wt% of 3-hydroxyoctadecanoate, between 0.1 wt% and 99 wt% of 3-hydroxyicosanoate, between 0.1 wt% and 99 wt% of 3-hydroxydocosanoate, between 0.1 wt% and 99 wt% of hydroxytetracosanoate, and between 0.1 wt% and 99 wt% of 3-hydroxyhexacosanoate.

All monomers of the mcl-PHAs used in the compositions of the invention comprise 6 or more carbon atoms, preferably between 6 and 40 carbon atoms. For example, all monomers of the mcl-PHAs used

in the compositions of the invention comprise between 6 and 36 carbon atoms, preferably between 8 and 34 carbon atoms. One of the monomers of the mcl-PHAs used in the compositions of the invention comprises 7 or more carbon atoms, and all monomers of said mcl-PHA comprise 6 or more carbon atoms, preferably between 6 and 40 carbon atoms, more preferably between 6 and 36 carbon atoms, more preferably between 6 and 28 carbon atoms.

Thus, the polyester backbone of mcl-PHAs used in the compositions of the invention includes an aliphatic pending group, usually in beta position (poly-3-hydroxy), with respect to the carbonyl unit. The polymers used in the composition of the invention can have a variety of molecular weights and molecular weight distributions, which is not critical to achieving the purposes of the invention. The polymers typically have a number averaged molecular weight over 300 Da, for example between 300 and 10^7 Da, and in a preferred embodiment between 10^3 and 10^4 Daltons. In a typical embodiment, the mcl-PHAs used in the mixtures of the invention have a number averaged molecular weight equal to or above 50,000 Da, preferable above 50,000 Da, for example, between 50,000 and 500,000 Da or between 50,000 and 440,000 Da or between 55,000 and 300,000 Da, for example, between 60,000 and 200,000 Da. Further typical number averaged molecular weights of the mcl-PHAs used in the mixtures of the invention is comprised between 60,000 and 200,000 Da, for example between 60,000 and 150,000 Da. Number averaged molecular weights (Mn) and polydispersity indices (Mw/Mn) were determined against PS standards by gel-permeation chromatography (GPC) using a Bruker 3800 equipped with a deflection RI detector. Tetrahydrofuran or Chloroform at 1 mL/min flow rate was used as eluent at room temperature.

Preferably, at least one of the mcl-PHAs used in the composition of the invention is of formula (II), or a stereoisomer thereof, wherein k is an integer comprised between 50 and 50,000. According to a further embodiment, n and m is an integer independently comprised between 10 and 8,000.

The mcl-PHAs used in the compositions of the invention can be either homopolymers or co-polymers, for example, copolymers of a 3-hydroxyalkanoate. Such mcl-PHAs can also comprise homopolymers wherein said mcl-PHA comprises an homopolymer of hydroxyalkanoate, for example comprising more than 8 carbon atoms, or more than 12 carbon atoms, or more than 16 carbon atoms, for example, between 8 and 40 carbon atoms or between 8 and 36 carbon atoms or between 9 and 30 carbon atoms.

In general, a mcl-PHA is formed by enzymatic polymerization of one or more monomer units inside a living cell. Examples of monomer units that can make the mcl-PHAs used in the compositions of the

invention include 3-hydroxyhexanoate, 3-hydroxyheptanoate, 3-hydroxyoctanoate, 3-hydroxynonanoate, 3-hydroxydecanoate, 3-hydroxyundecanoate, 3-hydroxydodecanoate, 3-hydroxytridecanoate, 3-hydroxytetradecanoate, 3-hydroxypentadecanoate, 3-hydroxyhexadecanoate, 3-hydroxyheptadecanoate, 3-hydroxyoctadecanoate, 3-hydroxynonadecanoate, 3-hydroxyicosanoate, 3-hydroxyhenicosanoate, 3-hydroxydocosanoate, 3-hydroxytricosanoate, 3-hydroxytetracosanoate, 3-hydroxypentacosanoate, 3-hydroxyhexacosanoate. The mcl-PHA can be a co-polymer of two or more, for example 2 or 3, of said monomers. For example, the mcl-PHA can be a co-polymer of poly-3-hydroxyhexanoate, e.g. poly(3-hydroxyhexanoate-co-3-hydroxyoctanoate) (PHOHHx). Examples of such mcl-PHA can be poly(3-hydroxyhexanoate-co-3-hydroxynonanoate) (PHNHHx), poly(3-hydroxyoctanoate) (PHO), poly(3-hydroxydecanoate) (PHD), or mixtures thereof.

Alternatively, the mcl-PHA can be an homopolymer of one of said monomers, for example, poly-3-hydroxyheptanoate, poly-3-hydroxyoctanoate, poly-3-hydroxynonanoate, poly-3-hydroxydecanoate, poly-3-hydroxyundecanoate, poly-3-hydroxydodecanoate, poly-3-hydroxytridecanoate, poly-3-hydroxytetradecanoate, poly-3-hydroxypentadecanoate, poly-3-hydroxyhexadecanoate, poly-3-hydroxyheptadecanoate, poly-3-hydroxyoctadecanoate, poly-3-hydroxynonadecanoate, poly-3-hydroxyicosanoate, poly-3-hydroxyhenicosanoate, poly-3-hydroxydocosanoate, poly-3-hydroxytricosanoate, poly-3-hydroxytetracosanoate, poly-3-hydroxypentacosanoate, poly-3-hydroxyhexacosanoate. The present invention also includes compositions comprising two or more, e.g. two three or four, mcl-PHAs.

It is also possible that the mcl-PHA of the invention comprises monomer units with carbon-carbon double bonds, e.g. 3-hydroxyocteneate, 3-hydroxydeceneate, 3-hydroxydodecenoate, 3-hydroxytetradecenoate, 3-hydroxydhexadecenoate, 3-hydroxyoctadecenoate, 3-hydroxyicosenoate, or mixtures thereof.

Proportions of mcl-PHA and polar polymer

The inventors have found that the mcl-PHA is a surprisingly good substitute of tackifying agents. The compositions of the invention thus encompass a wide range of mcl-PHA loads, depending on whether they are used as the only tackifying agent or in combination with further tackifying agents. For example, the amount of mcl-PHA in the composition can be at least 1 wt% with respect to the total weight of the composition, or between 1% and 60 wt%, preferably between 5% and 55 wt%, preferably between 5% and 50 wt%, preferably between 8% and 40 wt% with respect to the total weight of the

composition. For example, the amounts of mcl-PHA can be between 10% and 50 wt% with respect to the total weight of the composition, when no further tackifying agent is added. Alternatively, the amount of mcl-PHA can be as low as 1%, for example between 5% and 30 wt% with respect to the total weight of the composition, when combined with further tackifying agents.

Also the amount of polar polymer in the composition can be adjusted. Typical loads of polar polymer are more than 20 wt% with respect to the total weight of the composition, for example, between 35% and 70 wt% with respect to the total weight of the composition. Depending on whether the composition is formulated into a PSA or a hot melt or a HMPSA, the amounts of the polar polymer can be adjusted by the skilled person to achieve required specifications. For example, typical PSA compositions may comprise polar polymer in amounts between 35% and 80 wt%, or between 45% and 65 wt%, or between 35% to 70 wt%, or between 50% and 70 wt%, or between 52% and 62 wt%, with respect to the total weight of the composition, the vinyl content being typically comprised between 10% and 60%, for example between 20% and 50%. On the other hand, polar polymers are typically loaded in hot melt compositions in amounts between 35% and 70 wt% or between 40% and 70 wt% or 35% and 55 wt% with respect to the total weight of the composition, the vinyl content being typically comprised between 5% and 40%, e.g. between 10% and 40%. Furthermore, polar polymers are typically loaded in hot melt pressure sensitive adhesive compositions in amounts between 40% and 50 wt% between 35% and 55 wt% with respect to the total weight of the composition, the vinyl content being typically comprised between 5% and 60% or between 5% and 40%, e.g. between 10% and 40%.

Any of the proportions of mcl-PHA and polar polymer can be combined to make new ranges of components of compositions of the invention.

When the polar polymer or the mcl-PHA includes one or more chiral centers, the present invention includes mixtures of enantiomers or diastereoisomers, as well as enantiomerically pure compounds thereof. Thus, the present invention encompasses all possible isomers of a polar polymer or a mcl-PHA, "isomer" meaning species having atoms bonded in the same order but with different spatial distribution, for example, the present invention includes *cis*- and *trans*-isomers, *E*- and *Z*- isomers, R- and S- enantiomers, diastereomers, racemic mixtures thereof, or stereochemically enriched mixtures.

When a polymer is made of monomers including pending groups, the later can arrange in space in different orientations with respect to each other, a property known as "tacticity", which in the present application takes its normal meaning, and refers to the stereoregularity of the orientation of the pending groups with respect to the polymer's backbone. In isotactic polymers all the substituents are

located on the same side of the polymer's backbone. A 100% isotactic macromolecule consists of 100% meso diads. In syndiotactic polymers the substituents have alternating positions along the polymer's backbone. A 100% syndiotactic polymer consists 100% of racemo diads. Thus, the present invention encompasses both, isotactic and syndiotactic polymers, as well as intermediate situations between both, i.e. atactic polymers. An embodiment of the present invention includes a polar polymer which is isotactic or syndiotactic or atactic.

The components of the composition of the invention can be mixed following ordinary processes in the art such as those described in Encyclopedia of Polymer Science and Engineering, 2nd Ed., vol. 14, Polymer Blends chapter, page 9, 1988. Procedures well known to the skilled person are combining solutions of the composition components, by roller mixing or by compounding in an extruder or kneader and alike. In one embodiment, the mcl-PHA and the polar polymer are mixed, preferably in a high sheer mixer, at temperatures sufficient to melt the polymers, for example ranging from 20°C to 250°C, typically between 100°C and 200°C. Most compositions of the invention are mixed at a temperature comprised between 140°C and 190°C. Other additives in the formulation can be added before or after mixing mcl-PHAs and polar polymers

Adhesives

The compositions of the invention can act directly as Pressure sensitive adhesives (PSA), such as hot melt or hotmelt pressure sensitive adhesive, or can be formulated with further additives. The adhesive of the invention can be detached again from the substrate surfaces. Preferably, the pressure sensitive adhesives of the invention are used to reversibly bond two substrates or adherends. The hot melt and HMPSA adhesives of the invention may be used to bond a broad spectrum of different solid substrates. These substrates may be flexible or, alternatively, rigid. Preferably, one of the substrates to be bonded is thin and flexible, in the form more particularly of films, multi-layer films, paper, aluminum, or multi-layer constructions from paper, aluminium and polymer films.

The pressure sensitive and hotmelt pressure sensitive adhesives according to the invention can be used to bond substrates such as glass, metal, ceramic, wood, coated or uncoated paper, paperboard packaging and plastics, such as, for example, polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyamide (PA), polypropylene (PP) and polyethylene (PE), polyvinyl chloride (PVC) and polystyrene (PS). Thin flexible substrates such as films, multi-layer films or paper can then be glued to such solid substrates.

The adhesive composition of the invention is preferably used to bond plastic substrates, particularly

substrates made of polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyethylene terephthalate, polyamide, polyethylene naphthalate or cellophane. In a particular embodiment, the adhesive of the invention is used for reversible bonding of two flexible, two rigid or one flexible and one rigid substrates. The invention further provides the bonded, preferably reversibly bonded, substrates comprising the hot melt adhesive of the invention.

For example, the adhesive of the invention is used in the manufacture of packaging or parts of packaging such as lids, trays, containers, pouches, flow packs or blisters for food, pharmaceuticals, cosmetics as well as industrial applications. More particularly, the adhesive of the invention is used in the manufacture of resealable packaging or parts of resealable packaging for food products. The invention is also directed to the packaging or parts of packaging, such as lids, trays, containers, bags, pouches, flow packs or blisters, comprising the adhesive of the invention.

The above allows for many combinations depending on the properties required for each case, which can be adjusted by the skilled following the general principles herein described. For example, the composition can be an adhesive composition comprising

(i) a polyhydroxyalkanoate wherein one of the monomers of said polyhydroxylalkanoate comprises 7 or more carbon atoms, and all monomers of said polyhydroxylalkanoate comprise 6 or more carbon atoms, preferably at least 1 wt% of said polyhydroxyalkanoate with respect to the total weight of the composition;

(ii) more than 10 wt% with respect to the total weight of the composition of at least one of a copolymer of ethylene and vinyl acetate, a thermoplastic polyurethane, PVOH or a copolymer of ethylene and a (met)acrylate; and

(iii) optionally further components to complete the 100 wt% of the composition.

The compositions of the invention may display tack, for example above 5, or above 10 or above 20 KPa at 0°C as measured according to EN-14510:2005, or even at temperatures below 0°C. Thus, the compositions of the invention can be made into hot melt adhesives or PSA or HMPSA having tackiness at surprisingly low temperatures. The tack in all cases in the present application was measured according EN 14510:2005 wherein (see example 3 for details):

(a) 2 g of the sample were placed on a steel plate (7x7x0.01 cm) which was heated at 180ºC and then allowed to cool on a smooth surface to give a homogeneous film thickness;

(b) the sample was then introduced in a TA.XT2i Texture Analyzer (Stable Microsystems, Surrey, England) fitted with a thermally insulated chamber covered with aluminum, wherein temperature was controlled by an external thermocouple;

(c) the temperature was adjusted to the desired temperature of measurement and determined by a thermocouple placed in contact with the sample; and

(d) a cylindrical stainless steel rod or probe (3 mm diameter) with smooth flat end was used to measure the force necessary to separate it from the adhesive surface, the testing experimental conditions being the following:

- approach speed of the cylindrical probe to the sample: 0.1 mm/s
- force applied to the sample: 5 N
- time of application of the force: 1 s
- separation speed (pulling rate) of the cylindrical probe from the sample: 1 mm/s

Additives

The skilled person can choose among a wide variety of additives known in the art, for example, from Encyclopedia of Polymer Science and Engineering, 2nd Ed., vol. 14, p. 327-410, 1988 or other reference information. Hot melt and HMPSA compositions typically use waxes, and any which is compatible with the rest of the components of the mixture can be used in the present invention. The wax is added to the mixture in a amounts between 1 wt% and 40 wt% with respect to the total weight of the composition, for example between 5 wt% and 30 wt%, preferably between 10 wt% and 25 wt%. By way of example, the most popularly used waxes are paraffin waxes, microcrystalline waxes, Fischer-Tropsch synthetic waxes, and polyolefin (i.e. polyethylene, polypropylene, copolymers) waxes. Examples of types of waxes that may be used include natural waxes, partially synthetic waxes and fully synthetic waxes. Natural waxes are formed through biochemical processes and are mineral or products of animal or plant metabolism. Partially synthetic waxes are formed by chemically reacting natural waxes. Fully synthetic waxes are prepared by polymerizing low molar mass starting materials such as carbon, methane, ethane or propane. The two main groups of fully synthetic waxes are the Fischer-Tropsch waxes and polyolefin waxes such as polyethylene wax, polypropylene wax and copolymers thereof (see for example, Ullmann's Encyclopedia of Industrial Chemistry).

One of the main advantages of the invention is the fact that the mcl-PHA can be used as a tackifying agent, concretely as a tackifying agent in a PSA or hot melt composition. The adhesive compositions

of the invention may however comprise further tackifying agents in addition to the mcl-PHA. For example, the composition of the invention may comprise (i) between 10 and 95 wt%, e.g. 15-60 wt%, of a polar polymer, for example, of a copolymer of an unsaturated hydrocarbon and an (meth)acrylate ester or acid, or copolymer of unsaturated hydrocarbon and a vinyl saturated aliphatic ester, or a polyester, or a polyvinylacetate, or a thermoplastic polyurethane or mixtures thereof; and between 5 wt% and 80 wt% of a mcl-PHA; and comprises no tackifier.

Alternatively, the composition of the invention does comprise a further tackifying agent. For example, the further tackifying agent can be present in amounts up to 50 wt%, for example of 10–40 wt% or 15-35 wt% with respect to the total weight of the composition. These amounts can be reduced in the compositions of the invention, which may comprise between 0 and 40 wt% with respect to the total weight of the composition, for example between 0.1 and 30 wt% with respect to the total weight of the composition. For example, the composition of the invention may comprise (i) between 20 and 70 wt%, e.g. 30-65 wt%, of a copolymer of an unsaturated hydrocarbon and an acrylate ester or acid, or a copolymer of an unsaturated aliphatic hydrocarbon and a vinyl aliphatic ester, or a polyester, or a polyvinylacetate, or a thermoplastic polyurethane or mixtures thereof; and between 5 wt% and 40 wt% of a mcl-PHA; and (iii) between 10 wt% and 50 wt%, preferably between 10 wt% and 40 wt%, of a further tackifying agent.

The term “tackifier” or “tackifying agent” or “tackifying resin” is recognized in the art and includes those substances that provide tack to adhesive compositions. The tackifying agent is typically a resin and can be, but is not limited to, rosin resins, hydrocarbon resins, terpene resins and derivatives thereof.

The tackifying resin can be selected from rosin resins (also called colophony resins), rosin ester resins, fully or partly hydrogenated rosin resins, disproportionated rosin resins, fully or partly hydrogenated rosin ester resins, disproportionated rosin ester resins; aromatic, aliphatic or cycloaliphatic hydrocarbon resins, derivatives thereof, and fully or partly hydrogenated aromatic, aliphatic or cycloaliphatic hydrocarbon resins; terpene resins, terpene polymers and copolymers, phenol-modified terpene resins and hydrogenated derivatives thereof. For example, the tackifying resin is a hydrocarbon resin or a derivative thereof. Preferably, it is selected from aromatic, aliphatic or cycloaliphatic hydrocarbon resins, derivatives thereof, and fully or partly hydrogenated aromatic, aliphatic or cycloaliphatic hydrocarbon resins.

Although the skilled person can adjust the amount of said further tackifying agent, typically, the

adhesive composition comprises as further tackifying only a rosin resin or a derivative thereof, such as a fully or partly hydrogenated rosin resin, disproportionated rosin resin, a rosin ester resin, a fully or partly hydrogenated rosin ester resin or a disproportionated rosin ester resin. Preferably, only a rosin ester resin or a derivative thereof, such as a fully or partly hydrogenated rosin ester resin or a disproportionated rosin ester resin. More preferably, only a hydrogenated rosin ester resin, such as a glycerol ester of hydrogenated rosin.

The compositions of the invention may further comprise other additives frequently used in the preparation of PSA adhesives compositions. The adhesive composition of the invention can comprise one or more further additives. Preferably, the composition of the invention comprises 0 to 5 wt% of one or more further additives, based on the total weight of the composition. In a particular embodiment, it comprises 0.01 to 5 wt% of one or more further additives, preferably 0.01 to 3 wt. %, more preferably 0.05 to 2 wt. %, even more preferably 0.05 to 0.5 wt. %. Typical additives of hot melt or PSA adhesives are well known in the art. Examples of these additives include antioxidants, such as sterically hindered phenols, phosphites, thioethers or thioesters; stabilizers antislipping agents, such as amide derivatives; colorants, such as titanium dioxide; fillers, such as talc, clay, silica and calcium carbonate.

The composition of the invention can optionally include plasticizers (e.g., benzoates such as 1,4-cyclohexanedimethanol dibenzoate, glyceryl tribenzoate, or pentaerythritol tetrabenzoate, phthalates, paraffin oils, polyisobutylene, chlorinated paraffins, etc.). Suitable adhesives can be obtained with the compositions of the invention without the need of plasticizers. In a particular embodiment, the composition of the invention does not comprise plasticizers.

The composition of the invention does not require a plasticizer or a further tackifying agent, and the skilled person can decide not to use it if required.

However, depending on the final properties required, the composition of the invention may comprise 0.1 to 5 wt.% of at least one plasticizer, based on the total weight of the composition. Alternatively, the composition of the invention may comprise from 0.5 to 5 wt. %, for example from 1 to 5 wt. %, of at least one plasticizer. There are many plasticizers available to the skilled person. Some examples are medicinal white oils, mineral oils, vegetal or animal oils; alkyl esters of aliphatic or aromatic carboxylic acids, such as adipates, sebacates, phthalates, citrates, benzoates, mellitates and aromatic sulphonates; alcohols, glycols or polyols, including polyether polyols and polyester polyols; and mixtures thereof. A frequently used plasticizer appropriate in the present invention is an oil.

Preferably, it is selected from medicinal white oils (also called paraffin oils), mineral oils, vegetal oils and animal oils.

Preferably, the at least one plasticizer is a medicinal white oil, preferably a saturated mineral hydrocarbon, more preferably a saturated mineral hydrocarbon with a number molecular weight of 200 to 800 g/mol, even more preferably 500 g/mol. However said plasticizer can be selected from alcohols, glycols and polyols.

The compositions of the invention can also comprise as an optional additive 0.005 to 5 wt% of at least one antioxidant, based on the total weight of the adhesive composition, for example, 0.01 to 5 wt% of at least one antioxidant, preferably 0.01 to 3 wt%, more preferably 0.05 to 2 wt%, even more preferably 0.05 to 0.5 wt%. Said antioxidant can be selected from sterically hindered phenols, phosphites and mixtures thereof. Preferably, it is a mixture of a sterically hindered phenol and a phosphite. Sterically hindered phenols are well known to the skilled person in the art and refer to phenolic compounds which contain sterically bulky radicals, such as tert-butyl, in close proximity to the phenolic hydroxyl group thereof. In particular, they may be characterized by phenolic compounds substituted with tert-butyl groups in at least one of the ortho positions relative to the phenolic hydroxyl group. Hindered phenols frequently used have tert-butyl groups in both ortho-positions with respect to the hydroxyl group. Representative hindered phenols include pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl) benzene, n-octadecyl-3(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, 4,4'-rnethylenebis(4-rnethyl-6-tert-butylphenol), 4,4'-thiobis(6-tert-butyl-o-cresol), 6-(4-hydroxyphenoxy)-2,4-bis(n-ocytlthio)-1,3,5-triazine, 2,4, 6- tris(4-hydroxy-3,5-di-tertbutyl- phenoxy)-1,3,5-triazine, di-n-octadecyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, 2-(n-octylthio)ethyl-3,5-di-tert-butyl-4-hydroxybenzoate, and sorbitol hexa-(3,3,5-di-tert-butyl-4-hydroxy-phenyl) propionate.

Phosphites are preferably aromatically substituted phosphites, preferably substituted or unsubstituted triphenyl phosphites. Examples of these phosphites include triphenyl phosphite, trisnonylphenyl phosphite, and tris (2,4-di-tert butylphenyl)-phosphite.

For example, the composition of the invention may comprise 0.05 to 0.5 wt% of at least one antioxidant selected from sterically hindered phenols, aromatically substituted phosphites and mixtures thereof. Preferably, the antioxidant is a mixture of a sterically hindered phenol and an aromatically substituted phosphite, e.g. a mixture of pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) and tris (2,4-di-tert-butylphenyl)-phosphite.

Further additives that can be included in the compositions of the invention can be selected from the following:

- Stabilizers;
- fillers for reducing cost, adding bulk, improving cohesive strength (forming filler-matrix composite material with good interfacial properties) and altering properties; e.g., calcium carbonate, barium sulfate, talc, silica, carbon black, clays (e.g., kaolin);
- UV stabilizers which protect the material against degradation by ultraviolet radiation;
- pigments and dyes;
- biocides for hindering bacterial growth;
- flame retardants;
- antistatic agents:
- ferromagnetic particles, hygroscopic water-retaining materials, or other materials which can yield a composition which can be activated by microwave heating; and/or
- electrically conductive particles which can yield conductive hot-melt formulations.

The following examples provide illustrate specific embodiments of the application for further reference, and should not be taken in any case as limitative of the scope of the invention.

EXAMPLES

Glossary of terms

EVA: Ethylene vinyl acetate, VA: 18 wt% (6.68 molar%) IF: 150 g/10min (190°C, 2.16 Kg) ISO 1133

EVA: Ethylene vinyl acetate, VA: 28 wt% (11.25 molar%) IF: 400 g/10min (190°C, 2.16 Kg) ISO 1133

EVA: Ethylene vinyl acetate, VA: 33 wt% (13.83 molar%), IF: 15 g/10 min (190°C, 2.16 Kg) ISO 1133

EVA: Ethylene vinyl acetate, VA: 40 wt% (17.85 molar%), IF : 55 g/10 min (190°C, 2.16 kg) ISO 1133

EBA: ethylene n-butyl acrylate, % pp BA: 27 wt% (7.49 molar%), IF =150 g/10min (190°C, 2.16 Kg) ISO 1133

EBA: ethylene n-butyl acrylate, % pp BA: 33 (9.73 molar%), IF= 150 g/10min(190°C, 2.16 Kg) ISO 1133

Foralyn 90: hydrogenated rosin ester resin

Ibercer 3080: microcristalline paraffin wax

Piccolyte C115: polyterpene resin

Irganox™ 1010: Pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)

Example 1: mcl-PHAs

Different mcl-PHAs were prepared following the general procedure described below.

The biocatalyst used for the production of medium chain length polyhydroxyalkanoates (mcl-PHA) was *Pseudomonas putida* KT2440. The fermentations were performed in a 5-liters fermenter Braun Biostat B in two steps: a) 25 hours batch step followed by b) 33 hours pulse fed-batch step.

The bacteria were grown in 250 mL of Inoculum medium (Table 1) until reaching OD_{600nm} of 1.0. Two hundred mL of this culture were added to the fermenter already containing 2 L of production medium (Table 1).

Components	**Inoculum medium**	**Production medium**
Free fatty acids	5 g/L	10 g/L
$(NH_4)_2HPO_4$	4 g/L	1 g/L
$KH_2PO_4 \cdot 12H_2O$	6.67 g/L	4 g/L
Citric acid	0.8 g/L	0.8 g/L
$MgSO_4 \cdot 7\ H_20$	0.8 g/L	1.4 g/L
Trace elements solution (Table 2)	1 mL/L	10 mL/L

Table 1. Media Composition

	Final concentration (mM)
$FeSO_4 \cdot 7H_2O$	0.1
$CaCl_2 \cdot H_2O$	0.1
$ZnSO_4 \cdot 7H_2O$	0.01
$MnCl_2 \cdot 4H_2O$	0.1
$CoSO_4 \cdot 7H_2O$	0.1
$CuCl_2 \cdot 2H_2O$	0.01

Table 2. Composition of trace elements solution

Free fatty acids (FFA) were obtained by saponification of the raw material with KOH pH 10.0 at 65°C under constant stirring at 200 rpm. The mix was acidified with HCl (37% w/v) until pH 5.0. The organic fraction contained the FFA was removed, and kept for using during the fermentation. The proportion of FFA:glycerin was 91:9.

Fatty acid	Content in %
Palmitic acid (C16:0)	25.5 ± 0.6
Stearic acid (C18:0)	15.1 ± 0.5
Oleic acid (C18:1n9)	43.2 ± 0.1
Linoleic acid (C18:2n6)	12.0 ± 0.2

Table 3. Composition of the free fatty acids (FFA)

Conditions of culture:

- Batch step (25 hours):

30°C, stirring speed: 300-800 rpm, automatic adjusted to keep $\%pO_2$ constant and bubbling air at 1 vvm (gas volume per medium volume per minute). pH 7.0 was kept constant using H_2SO_4/NH_4OH during the first 8 h, and later NaOH was used.

- Fed-batch (33 hours):

NaOH was used to keep pH at 7.0.

At the beginning of this step 6.5 mL of 1.0M $MgSO_4 \cdot 7H_2O$ was added.

The feed is automatic to keep exponential growth measured as consume of O_2.

Extraction and purification of mcl-PHA

The cells are recovered by centrifugation at 8,000 g 10 minutes at 4°C and dried at 65°C until the dry weight remains constant.

PHA is extracted using chloroform as solvent in a Soxhlet system: 30-40 grams of dry biomass using 300 mL of solvent in a 250 mL-Soxhlet during 8 hours.

PHA-chloroform mixture is added to 10 volumes of cold methanol (4°C) which precipitates the polymer. mcl-PHA is recovered by centrifugation at 10,000 g 15 minutes. The pellet is washed with 1 volume of cold methanol and dried at room temperature using vacuum.

The exemplary mcl-PHAs tested had the composition indicated in Table 4.

	PHA-9	**PHA-15**	**PHA-19**	**PHA-24**
Mw (Da)	77,556	96,747	88,866	68,359
Mn (Da)	44,141	53,471	54,108	38,014
Mz	125,060	155,892	136,037	10,942
PD	1.73	1.81	1.64	1.79
3- hydroxyhexanoate	2.6	4.69	3.59	2.86
3- hydroxyoctanoate	19	26.91	26.19	25.95
3-hydroxydecanoate	31.5	28.93	33.39	34.94
3-hydroxydodecanoate	24	17.5	17.36	19.57
3-hydroxydodecenoate	0.7	3.3	1.8	1.45

3-hydroxytetradecanoate	11.8	5.18	4.4	4.36
3--hydroxytetradecenoate	8	12.51	11.3	10.22
3-hydroxyhexadecanoate	1.3	0.5	0.6	0
Tg (1F) ºC	-44	-50	-52	-49
Tg (2F) (ºC)	-48	-50	-52	-49

Table 4

Example 2: General procedure in bulk reactor

Each polar polymer and mcl-PHA were used in the proportions indicated in each case (Table 5 and Table 6). They were mixed at a time and temperature sufficient to obtain a homogeneous mixture, typically at 170°C and 100 rpm for 20 minutes. All compositions contain 0.5 wt% of Irganox™ 1010.

Comp. No. (Type)	EVA wt%	Vinyl Wt%	Foralyn 90 wt%	Piccolyte C115 wt%	mcl-PHA 9 wt%	mcl-PHA 15 wt%	mcl-PHA 19 wt%	mcl-PHA 24 wt%	Iberce r 3080 wt%
HOTMELT									
2 (Hotmelt)	49.75	18			29.75				20
4 (Hotmelt)	49.75	18				29.75			20
6 (Hotmelt) COMP.	39.75	18	39.75						20
7 (Hotmelt)	39.75	18	29.875			9.875			20
PSA									
11 (PSA) COMP.	59.75	40	39.75						
12 (PSA)	59.75	40			39.75				
13 (PSA)	59.75	40				39.75			
14 (PSA) COMP.	59.75	33	39.75						
15	59.74	40				39.75			
16(PSA)	59.75	40	29.875			9.875			
17(PSA)	59.75	40	19.875			19.875			
18 COMP.	59.75	40		39.75					
19 (PSA)	59.75	40					39.75		
20 (PSA)	59.75	40		29.875			9.875		
21(PSA)	59.75	40		19.875			19.875		
22 (PSA)	59.75	33						39.875	
22 (PSA)	59.75	33		19.875				19.875	
23 (PSA)	59.75	27		19.875				19.875	
24 EVA-PHB	59.75	40							

COMP.*									
25 EVA-PHB-Piccolyte COMP.**	59.75	40		19.875					
30 COMP.	0		39.75		59.75				
31 COMP.	0			39.75		59.75			

* Blend 24 has a 39.75 wt% content of 3-PHB

** Blend 25 has a 19.875 wt% content of 3-PHB

Table 5. EVA compositions of hot melts, PSAs and HMPSAs based on EVA

Comp. No. (Type)	EBA wt%	Vinyl Content	Foralyn 90 resin wt%	Piccolyte C115 Wt%	mcl-PHA 24 wt%
26 COMPARATIVE	59.75	27		39.75	
27	59.75	27			39.75
28	59.75	33		19.875	19.875
29	59.75	33			39.75

Table 6. PSA compositions based on EBA

Example 3: Measurement of tack

For the measurement of tack, a TA.XT2i Texture Analyzer (Stable Microsystems, Surrey, England) was used. Each sample was placed in a thermally insulated chamber covered with aluminum, wherein temperature can be controlled by an external thermocouple. Measurement of tackiness (also referred to as tack) was performed at the temperatures indicated below in Table 3, the temperature being determined by a thermocouple placed in contact with the sample.

Samples were prepared by depositing about 2 g of the obtained mixture on a steel plate (7x7x0.01 cm) which was heated at 180ºC and then allowed to cool on a smooth surface to give a homogeneous film thickness.

A cylindrical stainless steel probe (3 mm diameter) with smooth flat end was used to measure the force necessary to separate it from the adhesive surface. The testing experimental conditions were the following:

- approach speed of the cylindrical probe to the sample: 0.1 mm/s
- force applied to the sample: 5 N

- time of application of the force: 1 s

- separation speed (pulling rate) of the cylindrical probe from the sample: 1 mm/s

The results of the hot melt compositions tested are summarized in Table 7.

Sample HOTMELT	Tack max (KPa)	Temperature tack max.(ºC)	Peel Strength N/m	Brookfield viscosity at 180°C (mPa·s)
6 COMPARATIVE	1,284	80	341	4,500
2	200	40	120	4,000
4	300	45	200	2,800
7	650	50	330	3,000

Table 7

The results of the PSA compositions tested are summarized in Table 8.

	Measurements of Maximum tack		Measurements of tack at low temperatures	
Sample PSA	Maximum Tack (KPa)	Temperature of Maximum Tack (°C)	Low Temperature Tack (KPa)	Temperature at which the Low Temperature Tack has been Measured (°C)
18 COMPARATIVE	610	50	0	-20 to 45
21	1,174	20	200	-5
20	943	35	200	-15
19	400	10	200	0
Post-it commercial ref COMPARATIVE	20	25	0	-20 to 17
11 COMPARATIVE	493	40	0	-20 to 17
12	142	25	30	0
13	319	25	150	0
14	117	25	39	0
16	464	25	200	0
17	973	25	850	0
22	200	20	50	0
26 COMPARATIVE	500	50	0	-20 to 40
28	300	30	100	-5
29	200	20	40	0
27	200	15	120	-5
PHB	0	-20 to 80	0	-20 to 80

COMPARATIVE				
24 EV-PHB COMPARATIVE	508	65	0	-20 to 55
25 EV-PHB-Piccolyte COMPARATIVE	456	50	0	-20 to 40

Table 8

It should be noted that the compositions of the invention provide a comparable tack at room temperature. See the second column providing the temperature showing the maximum tack (Temperature of Maximum Tack) and the first column showing the tack at said temperature (Maximum Tack).

More importantly, the inventors tested the tack of the compositions of the invention at temperatures below room temperature. As it can be seen in column "Temperature at which the Low Temperature Tack has been Measured", these temperature ranges from -15 to 0°C. To their surprise, the compositions maintained a significant tack even at temperatures below 0°C. While, for example, comparative composition EV-PHB lost tack at 0°C, composition No. 17, wherein Piccolyte C115 had been entirely substituted with mcl-PHA 19, still displayed a significant tack at the same temperature. Even at -5°C, a temperature at which commercial PSA compositions lose their tack, the composition of the invention No. 19 still displayed a significant tack. Even in some cases, such as composition of the invention PSA7P, the temperature of maximum tack is below room temperature, which is a remarkable behavior in a PSA composition.

Example 4: peel strength at low temperature

Following the methods described in example 3, peel strength was measured at low temperature (below room temperature, from -20°C to 15°C) and room temperature. The results are shown in table 9:

Sample	**Peel Strength (N/m) Room temperature**	**Peel Strength (N/m) Low temperature**
18 COMPARATIVE	1,670	0
20	720	2,320
21	680	2,005
22	650	1,980
23	500	1,750
30	60	500

COMPARATIVE		
31 COMPARATIVE	75	620

The use of singular noun or pronoun when used with the term "comprising" in the claims and/or specification means "one", and also includes "one or more", "at least one", and "one or more than one". Throughout this application, the term "about" used to identify any values shown or appeared herein may be varied or deviated. The variation or deviation may be caused by errors of devices and methods used to determine a variety of values.

The terms "comprise", "have", and "include" are open-ended linking verbs. One or more forms of these verbs such as "comprise", "which comprise", "have", "which have", "include", "which include" are also open-ended. For example, any methods, which "comprise", "have", or "include" one or more steps, are not limited to possess only the one or those more steps, but also cover all unidentified steps.

Throughout the present invention weight percentage (“wt%”) is 100 times the relation in weight (e.g. in grams or kilograms) between the component specified and the total weight of the composition in the same units.

CLAIMS

1. A composition comprising

   (i) a polyhydroxyalkanoate wherein one of the monomers of said polyhydroxyalkanoate comprises 7 or more carbon atoms, and all monomers of said polyhydroxyalkanoate comprise 6 or more carbon atoms;

   (ii) more than 10 wt% with respect to the total weight of the composition of at least one polar polymer; and

   (iii) optionally further components to complete the 100 wt% of the composition.

2. An adhesive composition according to claim 1 comprising

   (i) a polyhydroxyalkanoate wherein one of the monomers of said polyhydroxylalkanoate comprises 7 or more carbon atoms, and all monomers of said polyhydroxylalkanoate comprise 6 or more carbon atoms;

   (ii) more than 10 wt% with respect to the total weight of the composition of at least one of a copolymer of ethylene and vinyl acetate, a thermoplastic polyurethane, PVOH or a copolymer of ethylene and a (met)acrylate; and

   (iii) optionally further components to complete the 100 wt% of the composition.

3. The composition according to the any of the previous claims wherein any monomer of the polyhydroxyalkanoate comprising 6 carbon atoms, is a 3-hydroxyalkanoate.

4. The composition according to the any of the previous claims wherein said polar polymer is selected from the group of copolymers of ethylene and vinyl acetate, copolymers of ethylene and a (met)acrylate, a thermoplastic polyurethane, PVOH and mixtures thereof.

5. The composition according to the any of the previous claims comprising more than 20 wt% of the polar polymer with respect to the total weight of the composition.

6. The composition according to the any of the previous claims comprising 35% to 70 wt% of the polar polymer with respect to the total weight of the composition.

7. The composition according to the any of the previous claims comprising between 1 wt% and 60 wt% of the polyhydroxyalkanoate with respect to the total weight of the composition.

8. The composition according to the previous claims which is a PSA adhesive.

9. The composition according to claim 8 comprising 40% to 70 wt% of the polar polymer with respect to the total weight of the composition.

10. The composition according to claim 9 wherein the vinyl content in the polar polymer is 10% to 60%.

11. The composition according to claims 1 to 5 which is a hot melt adhesive.

12. The composition according to claim 11 comprising 35% to 70 wt% of the polar polymer with respect to the total weight of the composition.

13. The composition according to claim 12 wherein the vinyl content in the polar polymer is 5% to 40%.

14. The composition according to the any of the previous claims wherein said polyhydroxyalkanoate comprises an homopolymer of polyhydroxyalkanoate.

15. The composition according to any of claims 1 to 13 wherein said polyhydroxyalkanoate is a mixture comprising the following monomers: between 0.1 wt% and 99 wt% of 3-hydroxyhexanoate, and at least one of between 0.1 wt% and 99 wt% of 3-hydroxyoctanoate, between 0.1 wt% and 99 wt% of 3-hydroxydecanoate, between 0.1 wt% and 99 wt% of 3-hydroxydodecanoate, between 0.1 wt% and 99 wt% of 3-hydroxytetradecanoate, between 0.1 wt% and 99 wt% of 3-hydroxyhexadecanoate, between 0.1 wt% and 99 wt% of 3-hydroxyoctadecanoate, between 0.1 wt% and 99 wt% of 3-hydroxyicosanoate, between 0.1 wt% and 99 wt% of 3-hydroxydocosanoate, between 0.1 wt% and 99 wt% of hydroxytetracosanoate, between 0.1 wt% and 99 wt% of 3-hydroxyhexacosanoate.

16. The composition according to any of the previous claims, wherein said polyhydroxyalkanoate is present in at least 1 wt% with respect to the total weight of the composition.

17. The composition according to any of the previous claims not having a crosslinker.

18. Use as a tackifying agent in an adhesive composition of a polyhydroxyalkanoate wherein one of the monomers of said polyhydroxylalkanoate comprises 7 or more carbon atoms, and all monomers of said polyhydroxylalkanoate comprise 6 or more carbon atoms.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/066990

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09J129/04 C09J133/08
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

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.
X,P	WO 2016/166292 A1 (REPSOL SA [ES]) 20 October 2016 (2016-10-20) examples 4-6, 14, 20, 21, 25; table 4	1,3,5-9, 11,14-18
Y	WO 2004/076583 A1 (METABOLIX INC [US]; WHITEHOUSE ROBERT S [US]) 10 September 2004 (2004-09-10) examples 10-12	1-18
Y	WO 96/05264 A1 (MINNESOTA MINING & MFG [US]) 22 February 1996 (1996-02-22) examples 1-96	1-18
A	WO 02/10303 A2 (3M INNOVATIVE PROPERTIES CO [US]; ABE HIDETOSHI [JP]; TAKAMATSU YORINO) 7 February 2002 (2002-02-07) table 1	1-18

☐ 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

"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
14 September 2017	02/10/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Scheunemann, Sven

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2017/066990

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2016166292 A1	20-10-2016	AR 104279 A1	12-07-2017
		WO 2016166292 A1	20-10-2016
WO 2004076583 A1	10-09-2004	AT 377060 T	15-11-2007
		AT 518932 T	15-08-2011
		DE 602004009764 T2	28-08-2008
		EP 1601737 A1	07-12-2005
		EP 1603987 A1	14-12-2005
		EP 1935945 A1	25-06-2008
		EP 2241605 A2	20-10-2010
		ES 2297385 T3	01-05-2008
		ES 2371069 T3	27-12-2011
		HK 1084687 A1	23-12-2011
		HK 1085504 A1	20-06-2008
		JP 4724111 B2	13-07-2011
		JP 5079321 B2	21-11-2012
		JP 5606966 B2	15-10-2014
		JP 2006518799 A	17-08-2006
		JP 2006519293 A	24-08-2006
		JP 2011140656 A	21-07-2011
		PT 1603987 E	10-11-2011
		US 2010305280 A1	02-12-2010
		WO 2004076582 A1	10-09-2004
		WO 2004076583 A1	10-09-2004
WO 9605264 A1	22-02-1996	AU 700073 B2	17-12-1998
		BR 9508583 A	14-07-1998
		CA 2195787 A1	22-02-1996
		DE 69515044 D1	16-03-2000
		DE 69515044 T2	08-06-2000
		EP 0775178 A1	28-05-1997
		ES 2141953 T3	01-04-2000
		JP H10504057 A	14-04-1998
		US 5614576 A	25-03-1997
		US 5753364 A	19-05-1998
		WO 9605264 A1	22-02-1996
WO 0210303 A2	07-02-2002	AU 7790201 A	13-02-2002
		JP 2002053835 A	19-02-2002
		WO 0210303 A2	07-02-2002