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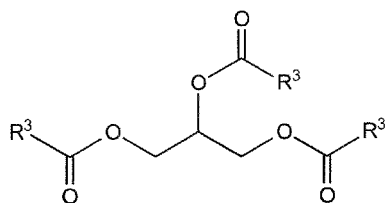
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(54) Title: ADHESIVE COMPOSITION AND BONDING METHODS



(A-2)

(57) Abstract: A one-component polyurethane adhesive composition useful for adhesively bonding lignocellulosic materials, comprising 75 wt% to 99.5 wt%, based on the total weight of the adhesive composition, of a prepolymer containing free isocyanate groups, and 0.5 to 25 wt%, based on the total weight of the adhesive composition, of an additive selected from one or more types of an ethylene glycol-based compound of the formula (A-1), one or more types of a glycerol triester of the formula (A-2), and from combinations thereof: R¹-O-[CH₂-CH₂-O]_n-R² (A-1) wherein: R¹ and R² are independently selected from C1-C6 alkyl, n is 1 or more; and R³ is, independently for each occurrence, a C1-C5 alkyl group.



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ADHESIVE COMPOSITION AND BONDING METHODS

The invention relates to the field of polyurethane (PUR) adhesives for lignocellulosic materials, in particular adhesives suitable for load-bearing engineered wood products such as glued laminated timber (GLT) or cross-laminated timber (CLT).

In the past decades, wood-based building materials were almost exclusively produced from coniferous wood species, predominantly spruce wood. As a result, the accompanying adhesive technology has focused and specialized on this type of wood. Due to climate change, wood pests and changing world markets, the availability of spruce wood is forecasted to decline strongly in the upcoming years. In parallel, there are politically driven attempts to shift to a low-CO₂ economy. Currently, the share of CO₂ from the worldwide production of building materials is estimated to be 40%. The main source is the energy-intensive production and transport of building materials based on steel, cement, glass or brick. Since building materials based on wood represent a low-CO₂ alternative, an increasing demand for wood-based building products can be expected.

Due to these changes in supply and demand, it becomes increasingly interesting to open up to previously neglected wood species, *i.e.*, beech, birch, ash, oak and teak, but also other lignocellulosic materials, *e.g.*, bamboo. For European wood, this includes, among others, coniferous species such as larch and Douglas fir, or deciduous species such as beech or birch. The use of such wood species requires that the corresponding adhesive technology is suitable. Currently, there is still a need for adjustment, especially with one-component polyurethane adhesives (1C-PUR). The widespread use of 1C-PUR adhesives in this field of application, especially in Europe, results from the short cycle times, the possibility to avoid the use of any solvent or water, and no need to mix two components. Alternative adhesive types used in the production of wood-based building materials are the water-borne phenol/resorcinol-formaldehyde (PF/RF/PRF) adhesives, melamine/urea-formaldehyde (MF/MUF) adhesives, and emulsion polymer-isocyanate (EPI) adhesives.

Due to the comparatively long process time with adhesives other than 1C-PUR adhesives and the associated costs, the types of wood mentioned above as alternatives to spruce wood are currently seldom utilized.

In order for an adhesive to be used for load-bearing building products in Europe, the adhesive has to fulfil a series of standardized tests. For 1C-PUR adhesives, these tests are described in the standards EN 302-1 to -8 [Refs. 1-8] together with the requirements described in
5 EN 15425 [Ref. 9]. In addition, also the standards for the final product have to be met, e.g., for GLT the EN 14080 [Ref. 10] or for CLT the EN 16351 [Ref. 11].

In such tests, especially delamination tests (EN 302-2), a failure of the adhesive joints has been observed when using 1C-PUR adhesive in combination with the previously mentioned
10 and neglected wood species. A main cause for this is dimensional changes in the wood initiated by fluctuations in humidity. Due to these deformations, high stresses arise within the wood. Since the individual boards deform differently, a stress peak occurs in the adhesive joint. If the adhesive is not able to compensate for the occurring stresses, the bond will fail. In technical jargon, such a failure is referred to as delamination. If such delamination exceeds the
15 threshold described in the respective standard, the adhesive, in combination with the use of a specific wood species, is considered not suitable for the application.

In order to be able to bond types of wood other than spruce wood as discussed above, Henkel & Cie. AG (Sempach Station, Switzerland) describe adhesive systems containing specific
20 primer compositions which can be used for a pre-treatment of surfaces to be bonded with 1C-PUR adhesives. Primer compositions are disclosed in this context, which comprise a water-soluble or dispersible surfactant and/or a water-soluble, dispersible or emulsifiable polyol ([Ref. 12]), or a compound selected from polyalkylene glycols, polyalkylene glycol monoethers and polyalkylene glycol diethers ([Refs. 13, 15 or 16]). These water-based primers can be sprayed
25 onto the wood before the adhesive is applied to reduce or avoid a failure in the adhesive joint described above. In addition, the functionality of primer systems relying on hydroxymethylated resorcinol (HMR) was studied in [Ref. 14].

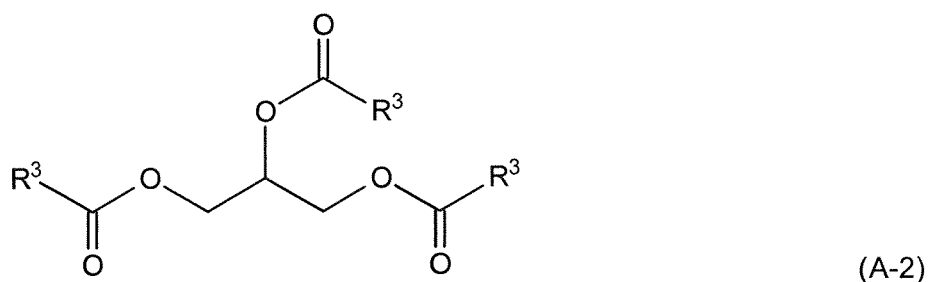
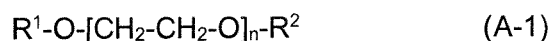
A disadvantage of this technical solution is the additional costs for the primer and for the
30 machinery required for its application. In addition, there is a certain increase in process times and a more complex production process, including additional potential for errors and failures. It has to be acknowledged that the primer only works in a very narrow band of specifications. As a result, this technical solution also only finds limited acceptance among manufacturers of wooden building products.

35 In [Ref. 17], an adhesive system is disclosed for bonding lignocellulosic articles, which comprises an organic polyisocyanate composition. Inert fatty acid esters, such as triglyceride

oils and, in particular, triglyceride oils having at least 33 carbon atoms, are disclosed as optional additives to dilute monomeric polyisocyanates of the adhesive system. [Ref. 18] discloses moisture-activated polyisocyanate adhesive compositions, which contain inert fatty acid esters as diluents, for which triglyceride oils, and in particular triglyceride oils having at least 33 carbon atoms, are also preferred.

In the context of the present invention, a different approach was taken by providing a one-component polyurethane adhesive including an additive that is able to enhance the compatibility of a lignocellulosic substrate with the adhesive. This technical solution can be exploited for the modification of existing 1C-PUR adhesives. Moreover, a 1C-PUR adhesive containing the additive can be used by a manufacturer of wood-based building materials, such as load-bearing engineered wood products, virtually without any adjustments to the existing production processes being required.

The invention thus encompasses, as a first aspect, a one-component polyurethane adhesive composition comprising 75 wt% to 99.5 wt%, based on the total weight of the adhesive composition, of a prepolymer containing free isocyanate groups, and 0.5 to 25 wt%, based on the total weight of the adhesive composition, of an additive selected from one or more types of an ethylene glycol-based compound of formula (A-1), one or more types of a glycerol triester of formula (A-2), and from combinations thereof:



wherein:

R^1 and R^2 are independently selected from C1-C6 alkyl, n is 1 or more; and R^3 is, independently for each occurrence, a C1-C5 alkyl group.

Further aspects of the invention relate to the use of the adhesive composition in accordance with the invention as an adhesive for lignocellulosic material, or to the use of the adhesive composition in accordance with the invention as an adhesive for the production of glued wood products.

A still further aspect of the invention relates to a method of adhesively bonding two or more lignocellulosic parts, said method comprising applying the adhesive composition in accordance with the invention to at least one surface of one lignocellulosic part and optionally one or more surfaces of one or more further lignocellulosic parts, and allowing the lignocellulosic parts to
5 adhere to each other via an adhesive bond.

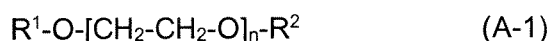
It has been found by the inventors that the incorporation of the additives of formula (A-1) and/or (A-2) into the adhesive composition provides for a better flow of the adhesive into the wood porous structure and penetrates the wood cell wall structure, plasticizing the amorphous wood biopolymers in the cell layers adjacent to the adhesive layer or bond line (Figure 1). Due to the
10 increased deformability of the wood, stresses in the region of the adhesive joint are better distributed. A stress peak that occurs locally in the adhesive joint is thus avoided, and eventually, delamination is minimized. This concept, according to which an adhesive for load-bearing timber construction specifically modifies the properties of the glued wood, has not been
15 used in the art, which previously focused on adapting the adhesive to the properties of the wood. The approach presented here creates the possibility for the 1C-PUR adhesive to circumvent its previous limitations by adapting the properties of the wood to form a sturdy bond. Thus, the concept creates the opportunity for an application with diverse types of wood, including the suitability for bonding hardwood, while relying on the advantages of the fast curing
20 of the 1C-PUR. In addition, the additive used is a biocompatible material which can be provided from renewable sources, e.g., in biorefineries, and which can be obtained at low costs.

As noted above, an aspect of the invention concerns a one-component polyurethane adhesive composition. The term “one-component polyurethane adhesive” or “one-component PUR
25 adhesive” is known and established. Equivalent terms are 1C-PUR adhesive, 1K-PUR adhesive, one-part polyurethane adhesive, and one-part PUR adhesive. In the following, the term “1C-PUR adhesive” shall be used for reasons of conciseness. As opposed to two-component PUR adhesives, which are comprised of resin and a hardener as separate components to be mixed by the user prior to or during the application, a 1C-PUR adhesive can
30 be applied by the user as a single component, thus facilitating the handling and the application of the adhesive. As will be appreciated by the skilled reader, the presence of the free isocyanate groups in the one-component polyurethane adhesive composition allows the composition to cure when it is in contact with moisture, such as atmospheric moisture or moisture already present in the lignocellulosic material. Hence, the one-component
35 polyurethane adhesive compositions providing free isocyanate groups are also known as moisture-curable polyurethane adhesive compositions.

The 1C-PUR adhesive composition in accordance with the invention comprises an additive selected from one or more types of the ethylene glycol-based compound of formula (A-1), one or more types of the glycerol triester of formula (A-2) and from combinations thereof. For reasons of conciseness, the additive selected from one or more types of the ethylene glycol-based compound of formula (A-1), one or more types of the glycerol triester of formula (A-2) and from combinations thereof shall also be referred to herein as “compatibilizing additive”. As a consequence of its incorporation as an additive into the adhesive composition in accordance with the invention, the compatibilizing additive is mixed in the composition with the prepolymer containing free isocyanate groups. As such, the compatibilizing additive can be conveniently applied as a part of the uncured 1C-PUR adhesive composition and simultaneously with the prepolymer. A separate application step, as it is required for a primer disclosed in the prior art discussed above, is not required.

As will be appreciated, the 1C-PUR adhesive composition may thus comprise, as the compatibilizing additive, one type of compound of formula (A-1), two or more types of compounds of formula (A-1), one type of compound of formula (A-2), two or more types of compounds of formula (A-2), or a combination of one or more types of the compound of formula (A-1) and one or more types of the compound of formula (A-2). It may also comprise one or more types of a compound of formula (A-1) and be free of a compound of formula (A-2), or may comprise one or more types of a compound of formula (A-2) and be free of a compound of formula (A-1). Preferably, the composition comprises one or more types of the compound of formula (A-1).

As noted above, the 1C-PUR adhesive composition may comprise, as an additive, one or more types of the ethylene glycol-based compound of formula (A-1):



wherein:

R^1 and R^2 are independently selected from C1-C6 alkyl and n is 1 or more. This one or more types of the ethylene glycol-based compound of formula (A-1) shall also be briefly referred to herein as the “ethylene glycol-based additive”.

R^1 and R^2 in formula (A-1) are preferably independently selected from methyl and ethyl, and are more preferably both methyl groups.

It is generally preferred that R^1 and R^2 are the same in formula (A-1).

The variable n in formula (A-1) indicates the number of units $-\text{CH}_2\text{-CH}_2\text{-O}-$ which are contained in a compound of the ethylene glycol-based additive under consideration. As noted above, n is 1 or more in the compounds providing the ethylene glycol-based additive. It will be understood that compounds with higher values of n can be suitably selected, or selected and combined, respectively.

In view of the simplicity of the formulation process which can be used to provide the adhesive composition, it may be expedient if the one or more types of the ethylene glycol-based compound of formula (A-1) are used as additive which are liquid at normal temperature and pressure (e.g., 20 °C and 1013 hPa) to facilitate the mixing of the compounds into the adhesive composition. As will be understood by the skilled person, this can be conveniently achieved, e.g., by keeping n , and thus the molecular weight of the compounds, at values where the compounds of formula (A-1) are in a liquid form. For example, the value(s) of n in the one or more types of compounds of formula (A-1) may be in the range of 1 to 21, preferably in the range of 1 to 16, and more preferably in the range of 1 to 11. However, the compounds of formula (A-1) are not limited to such values of n , since other formulation techniques can also be relied on, such as mixing the compounds of formula (A-1) into the adhesive composition at elevated temperatures above the melting point of the compounds of formula (A-1), or suitably combining higher molecular weight compounds of formula (A-1) and lower molecular weight compounds of formula (A-1) to inhibit crystallization and solidification of the compounds.

Generally, it is preferred that the number average molecular weight of one or more types of the compound of formula (A-1) is 1000 g/mol or less, more preferably 900 g/mol or less, and still more preferably 600 g/mol or less. As will be understood by the skilled reader, the reference to the number average molecular weight of one or more types of a compound of formula (A-1) refers to the number average molecular weight determined on the basis of all of the compounds of formula (A-1) contained in the composition. The number average molecular weight of one or more types of the compound of formula (A-1) can be conveniently determined by gel permeation chromatography (GPC), e.g., using polymer standards, such as polyethylene glycol standards, for calibration. While the measurement via GPC is also possible in the case where only one type of compound of formula (A-1) is used as the ethylene glycol-based additive, it will be understood that in this case the actual molecular weight of the concerned compound, which can be calculated based on the elemental composition thereof, can be used as the number average molecular weight.

An exemplary number average degree of polymerization, DP, expressed as the arithmetic average value of the number of repeating units n of the compounds of formula (A-1), is in the range of 1 to 21, preferably in the range of 1 to 19, and still more preferably in the range of 1 to 13. The average degree of polymerization can be calculated by dividing the number average molecular weight of the one or more types of compounds of formula (A-1), M_n , by the weight of the repeating unit $-\text{CH}_2\text{CH}_2\text{O}-$, *i.e.*, 44.05 g/mol. As noted above, the number average molecular weight can be conveniently determined via gel permeation chromatography, *e.g.*, using polymer standards, such as polyethylene glycol standards, for calibration. Alternatively, the number average degree of polymerization, DP, of the compounds of formula (A-1), can be determined via nuclear magnetic resonance (^1H NMR) by dissolving the compound in deuterated chloroform. The ratio between the area of the peaks of the ethylene units ($\text{CH}_2\text{CH}_2\text{O}$) – A: from 3.54 to 3.67 ppm – and, *e.g.*, the area of the peak of the methyl moiety (CH_3) in the ending groups – B: at 3.38 ppm and 1.21 ppm for R^1 and R^2 = methyl and ethyl ending groups, respectively – allows for the calculation of the number of repeating units n by using the following formula, *e.g.*, $n = 3A/2B$ for dimethyl terminated compounds, and $n = 3(A - B/3)/2B$ for diethyl terminated compounds.

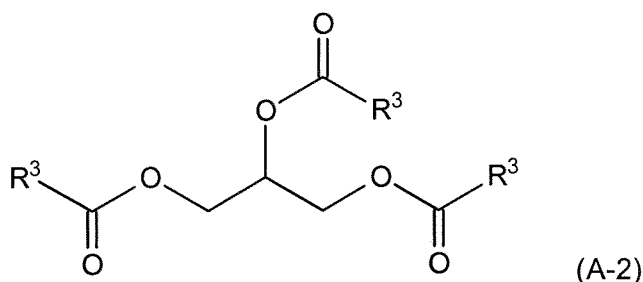
A variety of compounds of formula (A-1) are conveniently available as dialkylethers of mono-, di-, tri-, or tetraethylene glycol, which can be favourably used alone or as mixtures of two or more thereof as the compatibilizing additive or as a component thereof. As examples, reference can be made to a compound selected from ethylene glycol dimethyl ether ($n=1$), ethylene glycol diethyl ether ($n=1$), diethylene glycol dimethyl ether ($n=2$), diethylene glycol diethyl ether ($n=2$), triethylene glycol dimethyl ether ($n=3$), and tetraethylene glycol dimethyl ether ($n=4$). Thus, the one or more types of ethylene glycol-based compounds of formula (A-1) may comprise, or consist of, one or more types of compounds selected from ethylene glycol dimethyl ether ($n=1$), ethylene glycol diethyl ether ($n=1$), diethylene glycol dimethyl ether ($n=2$), diethylene glycol diethyl ether ($n=2$), triethylene glycol dimethyl ether ($n=3$), and tetraethylene glycol dimethyl ether ($n=4$).

Moreover, compounds of formula (A-1) are also conveniently available in the form of polyethylene glycol (PEG) di-C1-C6-alkyl ethers with various number average molecular weights, which can also be favourably used as the compatibilizing additive or as a component thereof in the context of the invention. Due to its production via a polymerization reaction, a PEG dialkyl ether may contain compounds of formula (A-1) which differ with respect to the number n of repeating units contained therein. Typically, a PEG dialkyl ether as referred to herein comprises at least one type of compound of formula (A-1) wherein n is 5 or more, without excluding the presence of compounds of formula (A-1) wherein n is less than 5. Thus,

in accordance with another preferred example, the one or more types of the ethylene glycol-based compound of formula (A-1) comprise or consist of a polyethylene glycol (PEG) dialkyl ether, e.g., a polyethylene glycol dialkyl ether having a number average molecular weight of 1000 g/mol or less, more preferably 900 g/mol or less, and most preferably 600 g/mol or less.

- 5 In such a polyethylene glycol dialkyl ether, R^1 and R^2 have the meanings and preferred meanings discussed above. Thus, a PEG dimethyl ether or a PEG diethyl ether are preferred, and most preferred is a PEG dimethyl ether, so that particular preference is given to a PEG dimethyl ether having a number average molecular weight of 600 g/mol or less. The lower limit of the average molecular weight is not particularly restricted, e.g., PEG dialkyl ethers with
10 number average molecular weights of 200 g/mol or more, or 250 g/mol or more may be used. For example, the ethylene glycol-based additive, or the compatibilizing additive as a whole, may essentially consist of, or consist of, a polyethylene glycol dialkyl ether as discussed above.

- As an alternative to or in addition to the ethylene glycol-based additive, the 1C-PUR adhesive
15 composition may comprise one or more types of the glycerol triester of formula (A-2) as an additive:



- 20 wherein:
 R^3 is, independently for each occurrence, a C1-C5 alkyl group, preferably a C1-C3 alkyl group. This one or more types of the glycerol triester of formula (A-2) shall also be briefly referred to herein as “glycerol ester-based additive”.
25 Preferably, R^3 is, independently for each occurrence, a C1-C3 alkyl group, and most preferably a methyl group. It is generally preferred that the three groups R^3 are the same.

- Thus, as preferred examples, the one or more types of a glycerol triester of formula (A-2) may comprise or consist of one or more, e.g., one, two or three, types of a glycerol triester selected
30 from glyceryl triacetate, glyceryl tripropanoate, and glyceryl tributyrates, and it is particularly preferred that the one or more types of the glycerol triester of formula (A-2) comprise glyceryl triacetate, or that the glycerol triester of formula (A-2) consists of glyceryl triacetate.

As a consequence of its incorporation as an additive into the adhesive composition in accordance with the invention, the compatibilizing additive selected from one or more types of the ethylene glycol-based compound of the formula (A-1), one or more types of the glycerol triester of the formula (A-2), and from combinations thereof, or their preferred forms as discussed herein, is admixed in, e.g., dissolved or dispersed in, the 1C-PUR adhesive composition in accordance with the invention, where it forms a mixture with the prepolymer containing free isocyanate groups. Thus, the compatibilizing additive can be homogeneously distributed in the composition. Typically, the compatibilizing additive cannot be identified as a separate phase in the 1C-PUR adhesive composition by visual inspection thereof with the naked eye, e.g., as droplets or aggregates. Preferably, the compatibilizing additive does not exhibit any concentration gradient within the adhesive composition. It has been found that the mixtures of the prepolymer containing free isocyanate groups and the compatibilizing additive as defined herein are advantageously stable. The components do not separate over extended periods of time.

The compatibilizing additive is comprised in the 1C-PUR adhesive composition in an amount of 0.5 to 25 wt%, based on the total weight of the adhesive composition (*i.e.*, % wt/wt). The lower limit of the comprised amount is preferably 1 wt%, more preferably 5 wt%. The upper limit is preferably 20 wt%, more preferably 15 wt%. Thus, the compatibilizing additive is preferably contained in the composition in an amount of 1 to 25 wt%, more preferably 1 to 20 wt%, still more preferably 5 to 20 wt%, and most preferably 5 to 15 wt%.

Without wishing to be bound by theory, it is assumed that the additive selected from one or more types of the ethylene glycol-based compound of the formula (A-1), one or more types of the glycerol triester of the formula (A-2), and from combinations thereof used in the adhesive compositions in accordance with the invention improves the compatibility of the adhesive with a lignocellulosic substrate. Since the compatibilizing additive does not act as an adhesive itself, the amount of the additive may be selected with a view to optimizing adhesive performance and/or costs of the adhesive composition.

In accordance with the above, very good results in terms of an increased adhesive performance and lower costs due to the availability of the compatibilizing additive can be achieved for a 1C-PUR adhesive composition in accordance with the invention, which comprises the compatibilizing additive.

Together with the additive selected from one or more types of the ethylene glycol-based compound of the formula (A-1), one or more types of the glycerol triester of the formula (A-2),

- and from combinations thereof incorporated therein as compatibilizing additive, the one-component polyurethane adhesive composition provided in accordance with the invention comprises a prepolymer containing free isocyanate groups, Such a prepolymer can be provided, for example, by relying on a one-component polyurethane adhesive composition as it is known in the art, including, e.g., 1C-PUR adhesives which are commercially available and into which the one or more types of the ethylene glycol-based compound of the formula (A-1) and/or one or more types of the glycerol triester of the formula (A-2) can be incorporated as an additive.
- 10 As optional constituents for the 1C-PUR adhesive composition in accordance with the invention, reference may be made, e.g., to one or more constituents selected from a filler, an activator or catalyst that promotes the curing reaction of the adhesive composition, and from other customary additives.
- 15 The NCO-content of the prepolymer containing free isocyanate groups is typically in the range of 5 to 30 wt%, based on the weight of the prepolymer, preferably 10 to 25 wt%, and more preferably 10 to 20 wt%, as determined, e.g., via titration according to DIN EN ISO 14896:2009 (Method B).
- 20 The number average molecular weight of the prepolymer is typically in the range of 400 to 5000 g/mol, preferably 750 to 1500 g/mol. It can be determined, e.g., according to EN ISO 13885-1:2021 via gel permeation chromatography using tetrahydrofuran as an eluent, or via NMR analysis.
- 25 The average NCO functionality of the prepolymer, *i.e.*, the average number of NCO functional groups in the molecules of the prepolymer, is typically in the range of 2.5 to 4.5, and preferably in the range of 3.0 to 4.0. It can be determined, e.g., via calculation from the NCO content and the number average molecular weight of the prepolymer.
- 30 Prepolymers containing free isocyanate groups for use in 1C-PUR adhesive compositions, also in the context of the present invention, are typically obtainable or obtained by reacting one or more types of compounds containing multiple isocyanate functional groups, such as polymeric methylene diphenyl diisocyanate (pMDI), as a polyisocyanate component, with one or more types of compounds containing multiple functional groups which are reactive with isocyanate groups. Preferred as such compounds that are reactive with isocyanate groups are compounds carrying two or more groups independently selected from a hydroxy group (-OH) and an amino group (-NH₂). As an example, reference can be made to a polyether polyol, *i.e.*,
- 35

a compound containing two or more repeating units linked by an ether bond, and further containing two or more, preferably two, hydroxy groups. Preferred polyether polyols, and thus preferred compounds which are reactive with isocyanate groups to provide a prepolymer for use in the context of the invention, are polyethylene glycol or polypropylene glycol. As another
5 example, reference can be made to a polyether polyamine, *i.e.*, a compound containing two or more repeating units linked by an ether bond and further containing two or more, preferably two, amino groups. Preferred polyether polyamines, and thus preferred compounds which are reactive with isocyanate groups to provide a prepolymer for use in the context of the invention, are a compound of the formula $\text{H}_2\text{N-R}^4\text{-O-PEG-O-R}^5\text{-NH}_2$, or a compound of the formula
10 $\text{H}_2\text{N-R}^4\text{-O-PPG-O-R}^5\text{-NH}_2$, wherein R^4 and R^5 are independently C1-C5 alkanediyl groups, -O-PEG-O- is a polyethylene glycol residue, and -O-PPG-O- is a polypropylene glycol residue.

The prepolymer containing free isocyanate groups, which is present in the 1C-PUR adhesive
15 in accordance with the present invention, is preferably a prepolymer that is obtainable or obtained by reacting a compound containing multiple isocyanate functional groups, preferably pMDI, and a polyether polyol containing two or more hydroxy groups, preferably a polyether polyol containing two hydroxy groups. The polyether polyol is preferably a polyether polyol which comprises ethylene glycol units, propylene glycol units or a combination of ethylene
20 glycol units and propylene glycol units as main repeating units, *i.e.*, in an amount of more than 50 mol%, based on the total number of repeating units of the polyether polyol. It is more preferred that the polyether polyol comprises ethylene glycol units, propylene glycol units or a combination of ethylene glycol units and propylene glycol units in an amount of 80 mol% or more, still more preferably 90 mol% or more, and most preferably the polyether polyol consists
25 of ethylene glycol units, propylene glycol units or a combination of ethylene glycol units and propylene glycol units.

In line with the above, a strongly preferred prepolymer for use in the 1C-PUR adhesive in accordance with the invention is a prepolymer containing free isocyanate groups which
30 consists of units obtainable or obtained by reacting pMDI with polyethylene glycol, polypropylene glycol, or with a combination of these glycols.

Suitable prepolymers containing free isocyanate groups are commercially available and methods for their preparation are known and described in the art, as summarized, *e.g.*, in [Ref.
35 15].

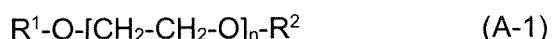
The one-component polyurethane adhesive composition comprises the prepolymer containing free isocyanate groups in an amount of 75 wt% to 99.5 wt%, based on the total weight of the adhesive composition. The lower limit of the comprised amount is preferably 80 wt%, more preferably 85 wt%. The upper limit is preferably 99 wt%, and more preferably 95 wt%. Thus, the content of the prepolymer is preferably 75 to 99 wt%, more preferably 80 to 99 wt%, still more preferably 80 to 95 wt% and most preferably 85 to 95 wt%.

The combined amounts of the prepolymer containing free isocyanate groups and the compatibilizing additive preferably account for 90 wt% or more, more preferably 95 wt% or more, and still more preferably 98 wt% or more of the one-component polyurethane adhesive composition in accordance with the invention, with the weight percentages being indicated on the basis of the total weight of the composition. The adhesive composition may consist of the prepolymer containing free isocyanate groups and the compatibilizing additive.

The adhesive composition in accordance with the invention preferably has a viscosity of 1 to 1000 Pa·s, more preferably of 5 to 500 Pa·s, and still more preferably of 10 to 100 Pa·s measured, e.g., at 25 °C using a rotational rheometer. As outlined in the examples below, the viscosity is preferably determined by frequency sweep experiments from 0.1 to 100 Hz performed with a rotational rheometer in a plate-plate configuration using disposable plates (25 mm diameter) of stainless steel. The sample can be placed with a gap size of $d = 0.1$ mm at 25 °C and under inert atmosphere, and deformations can be conducted at the shear strain value of $\gamma = 1\%$.

In line with the above, the following embodiments (i) to (iii) are listed as preferred embodiments of the invention:

(i) a one-component polyurethane adhesive composition comprising 80 to 99 wt%, more preferably 80 to 95 wt% and most preferably 85 to 95 wt%, based on the total weight of the adhesive composition, of a prepolymer containing free isocyanate groups, and 1 to 20 wt%, more preferably 5 to 20 wt%, and most preferably 5 to 15 wt%, based on the total weight of the adhesive composition, of one or more types of an ethylene glycol-based compound of formula (A-1) as an additive,



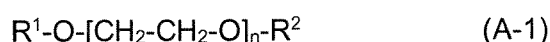
wherein:

R^1 and R^2 are independently selected from C1-C6 alkyl, n is 1 or more; and wherein the one or more types of the ethylene glycol-based compound of formula (A-1) comprise or consist of

one or more types of a compound selected from ethylene glycol dimethyl ether, ethylene glycol diethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether;

- (ii) a one-component polyurethane adhesive composition comprising 80 to 99 wt%,
 5 more preferably 80 to 95 wt% and most preferably 85 to 95 wt%, based on the total weight of the adhesive composition, of a prepolymer containing free isocyanate groups, and 1 to 20 wt%, more preferably 5 to 20 wt%, and most preferably 5 to 15 wt%, based on the total weight of the adhesive composition, of one or more types of an ethylene glycol-based compound of formula (A-1) as an additive,

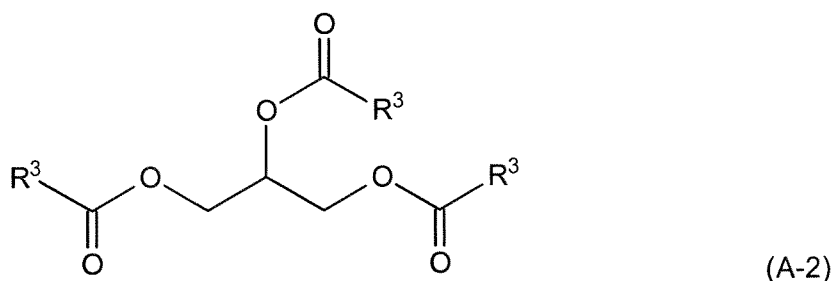
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wherein:

- R^1 and R^2 are independently selected from C1-C6 alkyl, n is 1 or more; and wherein the one
 15 or more types of the ethylene glycol-based compound of formula (A-1) comprise or consist of a PEG dimethyl ether with a number average molecular weight 1000 g/mol or less; and wherein the additive is comprised in the one-component polyurethane adhesive composition in an amount of 1 to 20 wt%, preferably 1 to 15 wt%, more preferably 5 to 15 wt%, based on the total weight of the adhesive composition;

- (iii) a one-component polyurethane adhesive composition comprising 80 to 99
 wt%, more preferably 80 to 95 wt% and most preferably 85 to 95 wt%, based on the total weight of the adhesive composition, of a prepolymer containing free isocyanate groups, and 1 to 20 wt%, more preferably 5 to 20 wt%, and most preferably 5 to 15 wt%, based on the total weight of the adhesive composition, of one or more types of a glycerol triester of formula (A-2)
 25 as an additive,



wherein:

- R^3 is, independently for each occurrence, a C1-C5 alkyl group.
 wherein the one or more types of a glycerol triester comprise or consist of one or more types of a glycerol triester selected from glyceryl triacetate, glyceryl tripropanoate, and glyceryl tributyrates.

Fillers, e.g., reinforcing fillers, suitable for use in 1C-PUR adhesive compositions are also known in the art as components of 1C-PUR adhesive compositions, and may also be contained in the compositions in accordance with the invention. Examples include titanium dioxide, silica, talc, and calcium carbonate.

An activator may be contained in the 1C-PUR adhesive composition in accordance with the invention in order to promote the curing reaction of the polyurethane if the prepolymer is in contact with moisture. Examples include tin carboxylates, organosilicon titanates, alkyl titanates, bismuth carboxylates, and dimorpholinodiethyl ether or alkyl-substituted dimorpholinodiethyl ethers.

Moreover, the 1C-PUR adhesive composition may comprise further additives in addition to the compatibilizing additive discussed above. Such additives are also known in the art, and may include, e.g., one or more selected from stabilizers, antioxidants, antimicrobial agents, UV-stabilizers, thixotropes and flameproofing agents.

As noted above, the 1C-PUR adhesive composition in accordance with the present invention has excellent compatibility with a broad variety of lignocellulosic materials and provides stable adhesive bonds between a variety of lignocellulosic substrates. These materials and substrates include wood or bamboo and include, in particular, lignocellulosic materials and substrates other than spruce wood, such as larch wood, Douglas fir wood, beech wood or birch wood.

Thus, the invention provides, as a further aspect, the use of the 1C-PUR adhesive composition as discussed herein as an adhesive for lignocellulosic material, preferably for a lignocellulosic material, which is at least one selected from wood or bamboo, and more preferably for wood which is at least one selected from larch wood, Douglas fir wood, beech wood and birch wood.

In this regard, it represents a clear advantage of the 1C-PUR adhesive composition in accordance with the invention that it can be applied and processed in the same way as 1C-PUR adhesive compositions known in the art, so that no adaptation or change of equipment is required for the production of glued wood products.

For example, the 1C-PUR adhesive composition in accordance with the invention provides an excellent performance when used as an adhesive for the production of glued wood products, preferably engineered wood products for structural purposes, and more preferably for glued

wood products selected from glued laminated timber, cross-laminated timber, I-beams, laminated beams and solid structural timber.

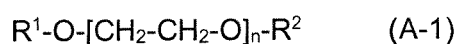
Also in this context, the advantages of the adhesive composition are pronounced if the glued wood products comprise wood selected from larch wood, Douglas fir wood, beech wood and birch wood.

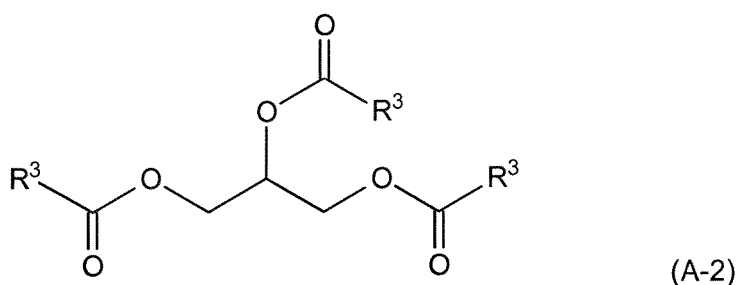
As a still further aspect, the invention provides a method of adhesively bonding two or more lignocellulosic parts, said method comprising applying the 1C-PUR adhesive composition in accordance with the invention to at least one surface of one lignocellulosic part and optionally one or more surfaces of one or more further lignocellulosic parts, and allowing the lignocellulosic parts to adhere to each other via an adhesive bond. By applying the adhesive composition wherein the compatibilizing additive is mixed with the prepolymer containing free isocyanate groups, the prepolymer and the compatibilizing additive can be simultaneously applied. Therefore, the separate application of a primer composition is not required. The application of the adhesive composition containing the prepolymer and the compatibilizing additive can be accomplished by a known coating operation, e.g., brushing or roll coating.

Typically, at least one, preferably all of the lignocellulosic parts to be bonded in the context of this method are made of wood or bamboo, and are preferably made of wood selected from larch wood, Douglas fir wood, beech wood and birch wood.

The following items summarize aspects of the invention. It will be understood that this summary forms a part of the description and supplements the information provided above, but that the details discussed above also continue to apply to the following summary.

1. A one-component polyurethane adhesive composition comprising 75 wt% to 99.5 wt%, based on the total weight of the adhesive composition, of a prepolymer containing free isocyanate groups, and 0.5 to 25 wt%, based on the total weight of the adhesive composition, of an additive selected from one or more types of an ethylene glycol-based compound of the formula (A-1), one or more types of a glycerol triester of the formula (A-2), and from combinations thereof:





wherein:

R^1 and R^2 are independently selected from C1-C6 alkyl, n is 1 or more; and

- 5 R^3 is, independently for each occurrence, a C1-C5 alkyl group.
2. The adhesive composition in accordance with item 1, wherein R^1 and R^2 are independently selected from methyl and ethyl.
- 10 3. The adhesive composition in accordance with items 1 or 2, wherein R^1 and R^2 are the same.
4. The adhesive composition in accordance with item 1, wherein R^1 and R^2 are both methyl.
- 15 5. The adhesive composition in accordance with any of items 1 to 4, wherein the number average molecular weight of the one or more types of the ethylene glycol-based compound of formula (A-1) is 1000 g/mol or less.
- 20 6. The adhesive composition in accordance with item 5, wherein the number average molecular weight of the one or more types of the ethylene glycol-based compound of formula (A-1) is 600 g/mol or less.
7. The adhesive composition in accordance with any of items 1 to 6, wherein the one or
 25 more types of the ethylene glycol-based compound of formula (A-1) comprise or consist of one or more types of a compound selected from ethylene glycol dimethyl ether, ethylene glycol diethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether.
- 30 8. The adhesive composition in accordance with any of items 1 to 7, wherein the one or more types of the ethylene glycol-based compound of formula (A-1) comprise or consist of a polyethylene glycol (PEG) dialkyl ether having a number average molecular weight of 1000 g/mol or less.

9. The adhesive composition in accordance with item 8, wherein the polyethylene glycol (PEG) dialkyl ether has a number average molecular weight of 600 g/mol or less.
- 5 10. The adhesive composition in accordance with any of items 1 to 9, which comprises one or more types of an ethylene glycol-based compound of the formula (A-1) as an additive, and which is optionally free of one or more types of a glycerol triester of the formula (A-2).
11. The adhesive composition in accordance with any of items 1 to 10, wherein R^3 is,
10 independently for each occurrence, a C1-C3 alkyl group.
12. The adhesive composition in accordance with any of items 1 to 11, wherein the three groups R^3 in formula (A-2) are the same.
- 15 13. The adhesive composition in accordance with item 12, wherein the glycerol triester of formula (A-2) is selected from glyceryl triacetate, glyceryl tripropanoate and glyceryl tributyrates and from combinations thereof.
14. The adhesive composition in accordance with item 13, wherein the glycerol triester of
20 formula (A-2) is glyceryl triacetate.
15. The adhesive composition in accordance with any of items 1 to 14, which comprises one or more types of a glycerol triester of the formula (A-2) as an additive, and which is optionally free of an ethylene glycol-based compound of the formula (A-1).
25
16. The adhesive composition in accordance with any one of items 1 to 15, which comprises the prepolymer containing free isocyanate groups in an amount of 75 to 99 wt%, and the additive selected from one or more types of an ethylene glycol-based compound of formula (A-1), one or more types of a glycerol triester of formula (A-2), and from combinations
30 thereof, in an amount of 1 to 25 wt%, based on the total weight of the adhesive composition.
17. The adhesive composition in accordance with item 16, which comprises the prepolymer containing free isocyanate groups in an amount of 80 to 99 wt%, and the additive selected from one or more types of an ethylene glycol-based compound of formula (A-1), one or more
35 types of a glycerol triester of formula (A-2), and from combinations thereof in an amount of 1 to 20 wt%, based on the total weight of the adhesive composition.

18. The adhesive composition in accordance with item 17, which comprises the prepolymer containing free isocyanate groups in an amount of 80 to 95 wt%, and the additive selected from one or more types of an ethylene glycol-based compound of formula (A-1), one or more types of a glycerol triester of formula (A-2), and from combinations thereof in an amount of 5 to 20 wt%, based on the total weight of the adhesive composition.
19. The adhesive composition in accordance with item 18, which comprises the prepolymer containing free isocyanate groups in an amount of 85 to 95 wt%, and the additive selected from one or more types of an ethylene glycol-based compound of formula (A-1), one or more types of a glycerol triester of formula (A-2), and from combinations thereof in an amount of 5 to 15 wt%, based on the total weight of the adhesive composition.
20. The adhesive composition in accordance with any of items 1 to 19, wherein the NCO-content of the prepolymer containing free isocyanate groups is in the range of 5 to 30 wt%, based on the weight of the prepolymer.
21. The adhesive composition in accordance with item 20, wherein the NCO-content of the prepolymer containing free isocyanate groups is in the range of 10 to 25 wt%, preferably 10 to 20 wt%.
22. The adhesive composition in accordance with any of items 1 to 21, wherein the number average molecular weight of the prepolymer containing free isocyanate groups is in the range of 400 to 5000 g/mol.
23. The adhesive composition in accordance with item 22, wherein the number average molecular weight of the prepolymer containing free isocyanate groups is in the range of 750 to 1500 g/mol.
24. The adhesive composition in accordance with any of items 1 to 23, wherein the average NCO functionality of the prepolymer containing free isocyanate groups is in the range of 2.5 to 4.5.
25. The adhesive composition in accordance with item 24, wherein the average NCO functionality of the prepolymer containing free isocyanate groups is in the range of 3.0 to 4.0.
26. The adhesive composition in accordance with any of items 1 to 25, wherein the prepolymer containing free isocyanate groups is obtainable by reacting a compound

containing multiple isocyanate functional groups with a polyether polyol containing two or more hydroxy groups.

27. The adhesive composition in accordance with item 26, wherein the compound
5 containing multiple isocyanate functional groups is polymeric MDI.

28. The adhesive composition in accordance with item 26 or 27, wherein the polyether
polyol comprises ethylene glycol units, propylene glycol units or a combination of ethylene
glycol units and propylene glycol units as main repeating units in an amount of more than 50
10 mol%, based on the total number of repeating units of the polyether polyol.

29. The adhesive composition in accordance with item 28, wherein the polyether polyol
consists of ethylene glycol units, propylene glycol units or a combination of ethylene glycol
units and propylene glycol units.
15

30. Use of an adhesive composition in accordance with any of items 1 to 29 as an adhesive
for lignocellulosic material.

31. The use in accordance with item 30, wherein the lignocellulosic material is at least one
20 selected from wood or bamboo.

32. The use in accordance with item 31, wherein the lignocellulosic material is at least one
material selected from larch wood, Douglas fir wood, beech wood and birch wood.

25 33. Use of the adhesive composition in accordance with any of items 1 to 29 as an adhesive
for the production of glued wood products.

34. The use in accordance with item 33, wherein the glued wood products are engineered
wood products for structural purposes, more preferably glued wood products selected from
30 glued laminated timber, cross-laminated timber, I-beams, laminated beams and solid structural
timber.

35. Use in accordance with any of items 33 or 34, wherein the glued wood products
comprise at least one type of wood selected from larch wood, Douglas fir wood, beech wood
35 and birch wood.

36. A method of adhesively bonding two or more lignocellulosic parts, said method comprising applying the adhesive composition in accordance with any of items 1 to 29 to at least one surface of one lignocellulosic part and optionally one or more surfaces of one or more further lignocellulosic parts, and allowing the lignocellulosic parts to adhere to each other via an adhesive bond.

37. The method in accordance with item 36, wherein the lignocellulosic parts are made from at least one material selected from wood or bamboo.

38. The method in accordance with item 37, wherein the lignocellulosic parts are made from at least one wood selected from larch wood, Douglas fir wood, beech wood and birch wood.

Examples

The following examples serve as an illustration of the invention.

The following two substances were used as exemplary additives:

- Glyceryl triacetate (GTA) – $m_w = 218$ g/mol
CAS-No: 102-76-1; ($\geq 99.0\%$); Merck KGaA (Darmstadt, Germany)
- Polyethylene glycol dimethyl ether (diMePEG) – $M_n = 250$ g/mol
CAS-No: 24991-55-7; ($\geq 99\%$); Merck KGaA (Darmstadt, Germany)

In addition, the following substance was used as an additive in comparative tests:

- Rapeseed oil (RO) – $\overline{m_w} = 879$ g/mol
CAS-No: 8002-13-9; Allgäuer Ölmühle e.K. (Kempten, Germany)
(triglyceride oil predominantly esterified with C18 fatty acids)

For the additives to be mixed, the following commercially available 1C-PUR adhesive was used:

- LOCTITE® HB S309 PURBOND
Henkel & Cie. AG (Sempach Station, Switzerland)

The modified adhesives (according to the invention including GTA or diMePEG, and for comparative purposes including RO) were produced by adding one of the three substances in the indicated mass fractions to the commercially available 1C-PUR adhesive. To ease the

visibility during further testing, a red fluorescent perylene-based dye was added to each mixture in a quantity of 0.05% (w/w), as well as to the commercial 1C-PUR adhesive, which was used for comparison:

- Fluorescent Red (Article No. 94720)

5 CAS-No: 335282-25-2; (100%); Kremer Pigmente GmbH & Co. KG
(Aichstetten, Germany)

From each mixture and the commercially available 1C-PUR adhesive, batches of approx. 200 g were prepared under identical conditions. Therefore, the commercially available 1C-
10 PUR adhesive, the colorant, and the additive were weighed in and the container was closed under a nitrogen atmosphere. For mixing, the closed container was placed in a desiccator, with an agitator entering through an opening with a special seal in the lid. Just when placing the lid onto the desiccator, the container with the weighed-in substances was opened and the agitator was placed inside. Then, the desiccator was evacuated while homogenizing the mixture for 30
15 min. After mixing, the container with the substances was removed and sealed airtight until being used.

Following the procedure of EN 302-1, longitudinal tensile shear specimens were produced with $n=10$ specimens from beech wood for each of the tests of the tensile shear strength under the
20 test conditions "A1" or "A4". Special care was taken to use wood boards with very little variation, exceeding the requirements of the standard. For comparative examples, the wood was sprayed either with 20 g/m² of either water or one of two waterborne primer solutions containing 10%wt of PEG with a molar mass of 600 g/mol or the above introduced diMePEG. In addition to the standardized procedure of EN 302-1, the deformation in the overlapping
25 region of the shear strength specimen was recorded during testing. Therefore, a random dot pattern was added to the area of interest in the overlapping region of the shear strength specimen. All specimens were mechanically measured in the tensile shear mode in a universal testing machine with wedge screw specimen holders (ZwickRoell GmbH & Co.KG, Ulm, Germany) at a constant displacement rate of 0.7 mm/min, and the maximum force was
30 measured, allowing for the determination of the tensile shear strength (τ_m).

For the observation and evaluation of the deformation, an "ARAMIS 12M" (GOM, Braunschweig, Germany) equipment, which consists of a set of stereo-cameras, and the digital image correlation software "GOM Correlate Pro" were used. The software calculates the local
35 shear angle and plots it depending on the distance to the centre of the bond line.

The performance of the modified and the original 1C-PUR adhesive composition was compared on bonded specimens, and reference samples with water and two primers based on PEG and diMePEG were analysed. Moreover, a set of samples containing vegetable oil – rapeseed oil, RO was prepared to carry out comparative tests.

5

Viscosity measurements were carried out via frequency sweep experiments from 0.1 to 100 Hz, performed with a rotational rheometer (MCR 301 rheometer, Anton Paar Group AG, Graz, Austria) in a plate-plate configuration using disposable plates (25 mm diameter) of stainless steel. The sample was placed with a gap size of $d = 0.1$ mm at 25 °C and under inert
10 atmosphere, and deformations were conducted at the shear strain value of $\gamma = 1\%$.

Figure 2 shows A) the complex viscosity and B) the relative complex viscosity values at 25 °C and $f = 1$ Hz for adhesive compositions containing 0%, 1%, 2%, 5%, 10% or 20% (% wt/wt) of the additives GTA or diMePEG, and the corresponding fits to the data.

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Under the standard's test conditions "A1" (7 days conditioning at 20 °C/65% RH and mechanically tested in dry conditions), all samples show strength values (τ_m) above the benchmark value of 10 MPa (Figure 3A). Moreover, adhesives with additives in accordance with the invention show a narrower distribution with similar or higher average values than those
20 without additives in the formulation (15-17 MPa for additives vs. 13-15 MPa for primers). The force density (f) (Figure 3B) is higher for those adhesives with additives (110-150 GN/m³) than without any additive (70-100 GN/m³) due to the thinner bond line values for samples glued with the adhesives containing additives (100-140 μ m for additives vs 150-210 μ m for primers). The bond line apparent shear modulus (G_{app}) is also higher for those samples with additives in the
25 composition (0.6-1.1 GPa for additives vs. 0.3-0.6 GPa for primers), indicating that the resulting cured network has fewer defects, penetrates better and sees better the influence of the wood in the interphase due to a reduction in the bond line thickness (Figure 3C). Finally, the wood failure (WF), adhesive failure (AF) and cohesive failure (CF) percentages for the different adhesives vary from 27% to 47%, from 25% to 55%, and from 4% to 41% with no clear
30 correlation (Figure 3D). It should be emphasized that identifying the AF and CF percentages for the thin samples obtained when gluing with adhesives containing additives was difficult. Therefore, using such additives in the 1C-PUR adhesive composition enhances the mechanical properties and performance of the bond line network. The results illustrated in Fig. 3 for samples in accordance with the invention (marked as "PUR-additive") were obtained for
35 adhesive compositions containing 5% (wt/wt) of the respective additives in the 1C-PUR adhesive. As noted above, comparative examples marked as "PUR-primer" used the 1C-PUR

adhesive without an additive, and were prepared by applying water or a primer selected from PEG and diMePEG onto the surface.

The deformation analysis in the overlapping area at constant stress value ($\tau = 4$ MPa) showed that with the presence of an additive in the adhesive composition, the maximum deformation in the bond line is reduced, together with a broadening of the strain distribution (Figure 4A and 4B). Therefore, this is a clear indication that i) the cured network is stronger and ii) strain is transferred to the solid wood due to a better matching of the mechanical properties of both the cured adhesive and wood. Moreover, the same analysis at a constant strain value ($\gamma = 0.01$) shows how the presence of an additive induces a transfer of deformations beyond the interphase to the remaining wood structure (Figure 4C and 4D). Thus, the use of additives reduces the viscosity of the final composition, allowing better penetration of the adhesive into the wood structure and transferring the deformation to the bulk wood regions due to the swelling/plasticization of the wood cell wall structure in the interphase. The results illustrated in Fig. 3 for samples in accordance with the invention (Fig. 4B and 4D) were likewise obtained for adhesive compositions containing 5% (wt/wt) of the respective additives in the 1C-PUR adhesive. As noted above, comparative examples (Fig. 4A and 4C) used the 1C-PUR adhesive without an additive, and were prepared by applying water or a primer selected from PEG and diMePEG onto the surface.

Figure 5 shows the average bond line thickness, which was evaluated by taking pictures covering 8 cm of the bond line with an LCD digital light microscope (Mustool G1200D, China) with a 1920x1080 pixels resolution, and a 1200X maximum magnification. Pictures were processed to obtain the perpendicular shape profile to the bond line using ImageJ 1.51j8 software, and the peak profiles were analyzed using ImageJ 1.51j8 and using OriginPro® 2021 software with a Pseudo-Voigt function. The average bond line thickness for each picture was calculated from the full width at half maximum (FWHM) of the peak signal. The mean bond line value and the corresponding standard deviation were calculated from 20 analyzed bond lines.

Under the standard's test conditions "A4" (7 days conditioning at 20 °C/65% RH, 6 h in boiling water, 2 h in water at 20 °C, and mechanically tested in wet conditions), all samples containing 5% (wt/wt) and 10% (wt/wt) additives in accordance with the invention (GTA, diMePEG) in the 1C-PUR adhesive composition show strength values (τ_m) above the benchmark value of 6 MPa (Figure 6) while samples with no additives in the composition – pure 1C-PUR adhesive – failed in average and did not pass the A4 test. The minimum τ_m value defined for 1C PUR adhesives in EN 15425 (2017) is 6 MPa for A4 testing, which is marked with a dashed line in Fig. 6. Similarly, samples using rapeseed oil (RO) as an additive in the 1C-PUR composition in

amounts of 5% (wt/wt) and 10% (wt/wt), respectively, did not pass. Therefore, using the additives as defined herein in the 1C-PUR adhesive composition enhances the mechanical properties and performance of 1C-PUR in wet conditions.

5 Description of Figures:

Figure 1 presents a scheme representing how the additive diffuses from the adhesive into the wood cell wall when curing and at the same time helps the penetration of the adhesive into the wood structure.

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Figure 2 shows A) the complex viscosity and B) the relative complex viscosity values at 25 °C and $f = 1$ Hz for adhesive compositions containing different concentrations of additives (% wt/wt, GTA or diMePEG), and the corresponding fits to the data.

15 Figure 3 shows A) shear strength values (τ_m), B) force density values (f), C) apparent shear modulus (G_{app}), and D) wood, adhesion, and cohesion failure (WF, AF, and CF) percentages for the samples glued with 1C-PUR adhesive with water treatment (comparative example) or a prior priming step (diMePEG or PEG, comparative examples), and the two modified 1C-PUR compositions with 5% of additives (GTA and diMePEG) in A1 testing (after 7 days conditioning
20 at 20 °C/65% RH, and mechanically tested in these conditions). *Note:* $n=10$ (all symbols are the average, and the error bars are the standard deviation).

Figure 4 shows average shear strain deformation values (γ) at the shear strength value of $\tau = 4$ MPa for 1C-PUR adhesives with A) primers – *i.e.*, water, PEG and diMePEG - or B) additives
25 – *i.e.*, GTA and diMePEG - showing a higher concentration of deformation in the bond line for the adhesives without additives. C) Average shear strain deformation values (γ) at the shear strain value of $\gamma = 0.01$ for 1C-PUR adhesives with primers – *i.e.*, water, PEG and diMePEG - or D) additives – *i.e.*, GTA and diMePEG - showing a better deformation distribution along the wood-interphase-bond line for the additives-containing adhesives and indicating better transfer
30 of deformations and stresses compared with the adhesive without additives in the compositions in A1 testing (after 7 days conditioning at 20 °C/65% RH, and mechanically tested in these conditions). *Note:* $n=10$.

Figure 5 compares the adhesive bond line thickness after curing and using primers, *i.e.*, water
35 (empty circle), PEG (empty square), and diMePEG (empty diamond), or additives (concentration 5% wt/wt), *i.e.*, GTA (filled circle), and diMePEG (filled diamond)

Figure 6 shows shear strength values (τ_m) for the samples glued with 1C-PUR adhesive with water treatment (comparative example) and samples glued with 1C-PUR adhesive containing rapeseed oil as an additive (RO, 5% and 10%, each wt/wt, comparative example), and two modified 1C-PUR compositions in accordance with the invention with 5% and 10% of additives (wt/wt, GTA and diMePEG) in A4 testing (after 7 days conditioning at 20 °C/65% RH, 6 h in boiling water, 2 h in water at 20 °C, and mechanically tested in wet conditions). *Note: n=10 (all symbols are the average, and the error bars are the standard deviation).*

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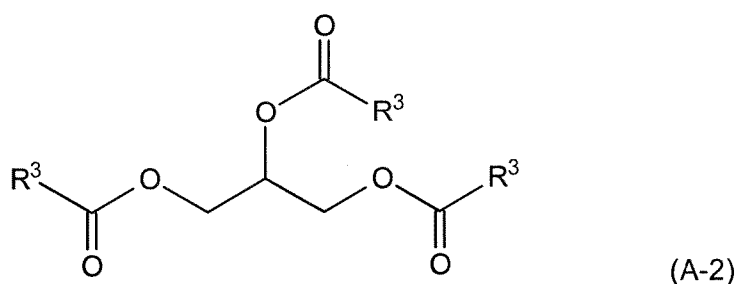
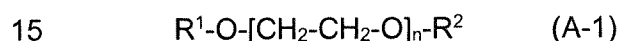
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Claims

1. A one-component polyurethane adhesive composition comprising:
 75 wt% to 99.5 wt%, based on the total weight of the adhesive composition, of a prepolymer
 10 containing free isocyanate groups, and 0.5 to 25 wt%, based on the total weight of the adhesive
 composition, of an additive selected from one or more types of an ethylene glycol-based
 compound of the formula (A-1), one or more types of a glycerol triester of the formula (A-2),
 and from combinations thereof:



wherein:

- 20 R^1 and R^2 are independently selected from C1-C6 alkyl, n is 1 or more; and
 R^3 is, independently for each occurrence, a C1-C5 alkyl group.

2. The adhesive composition in accordance with claim 1, wherein R^1 and R^2 are
 independently selected from methyl and ethyl.

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3. The adhesive composition in accordance with claim 1 or 2, wherein the one or more
 types of the ethylene glycol-based compound of formula (A-1) comprise one or more types of
 a compound selected from ethylene glycol dimethyl ether, ethylene glycol diethyl ether,
 diethylene glycol dimethyl ether, diethylene glycol diethyl ether, triethylene glycol dimethyl
 30 ether, and tetraethylene glycol dimethyl ether.

4. The adhesive composition in accordance with any of claims 1 to 3, wherein the one or
 more types of the ethylene glycol-based compound of formula (A-1) comprise a polyethylene
 glycol dialkyl ether having a number average molecular weight of 1000 g/mol or less.

5. The adhesive composition in accordance with any of claims 1 to 4, wherein R^3 is, independently for each occurrence, a C1-C3 alkyl group.

5 6. The adhesive composition in accordance with any of claims 1 to 5, wherein the three groups R^3 in formula (A-2) are the same.

7. The adhesive composition in accordance with any of claims 1 to 6, which comprises the prepolymer containing free isocyanate groups in an amount of 80 to 95 wt%, and the
10 additive selected from one or more types of an ethylene glycol-based compound of formula (A-1), one or more types of a glycerol triester of formula (A-2), and from combinations thereof in an amount of 5 to 20 wt%, based on the total weight of the adhesive composition.

8. The adhesive composition in accordance with any of claims 1 to 7, wherein the
15 prepolymer containing free isocyanate groups is obtainable by reacting a compound containing multiple isocyanate functional groups with a polyether polyol consisting of ethylene glycol units, propylene glycol units or a combination of ethylene glycol units and propylene glycol units.

9. Use of an adhesive composition in accordance with any of claims 1 to 8 as an adhesive
20 for lignocellulosic material which is at least one selected from larch wood, Douglas fir wood, beech wood and birch wood.

10. Use of the adhesive composition in accordance with any of claims 1 to 8 as an adhesive
25 for the production of glued wood products.

11. The use in accordance with claim 10, wherein the glued wood products are engineered
wood products for structural purposes, preferably glued wood products selected from glued laminated timber, cross-laminated timber, I-beams, laminated beams and solid structural
timber.

30 12. Use in accordance with any of claims 10 or 11, wherein the glued wood products comprise at least one type of wood selected from larch wood, Douglas fir wood, beech wood and birch wood.

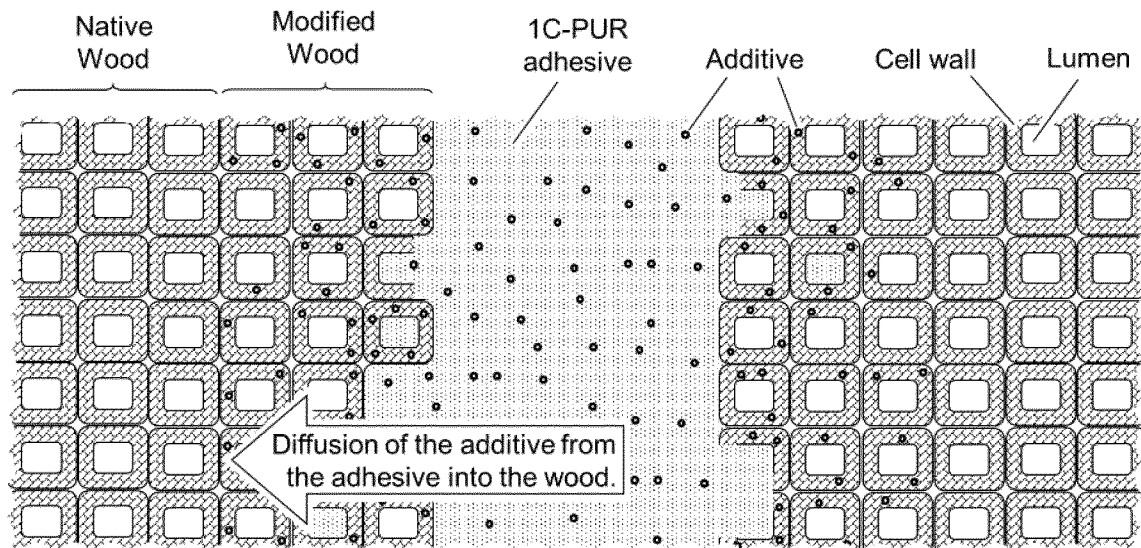
35 13. A method of adhesively bonding two or more lignocellulosic parts, said method comprising applying the adhesive composition in accordance with any of claims 1 to 8 to at least one surface of one lignocellulosic part and optionally one or more surfaces of one or more

further lignocellulosic parts, and allowing the lignocellulosic parts to adhere to each other via an adhesive bond.

14. The method in accordance with claim 13, wherein the lignocellulosic parts are made
5 from wood or bamboo.

15. The method in accordance with claim 14, wherein the lignocellulosic parts are made from at least one wood selected from larch wood, Douglas fir wood, beech wood and birch wood.

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**Fig. 1**

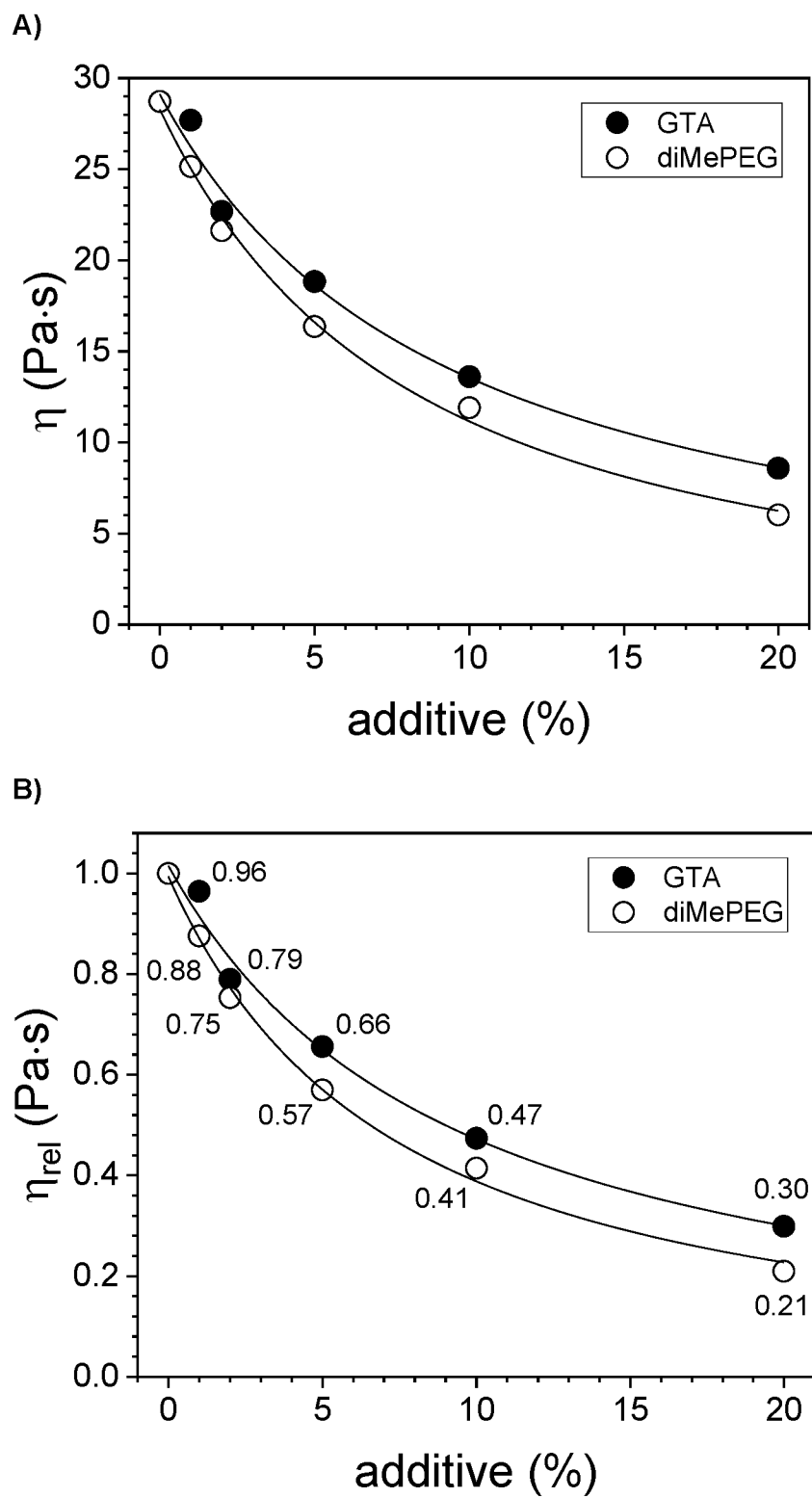


Fig. 2

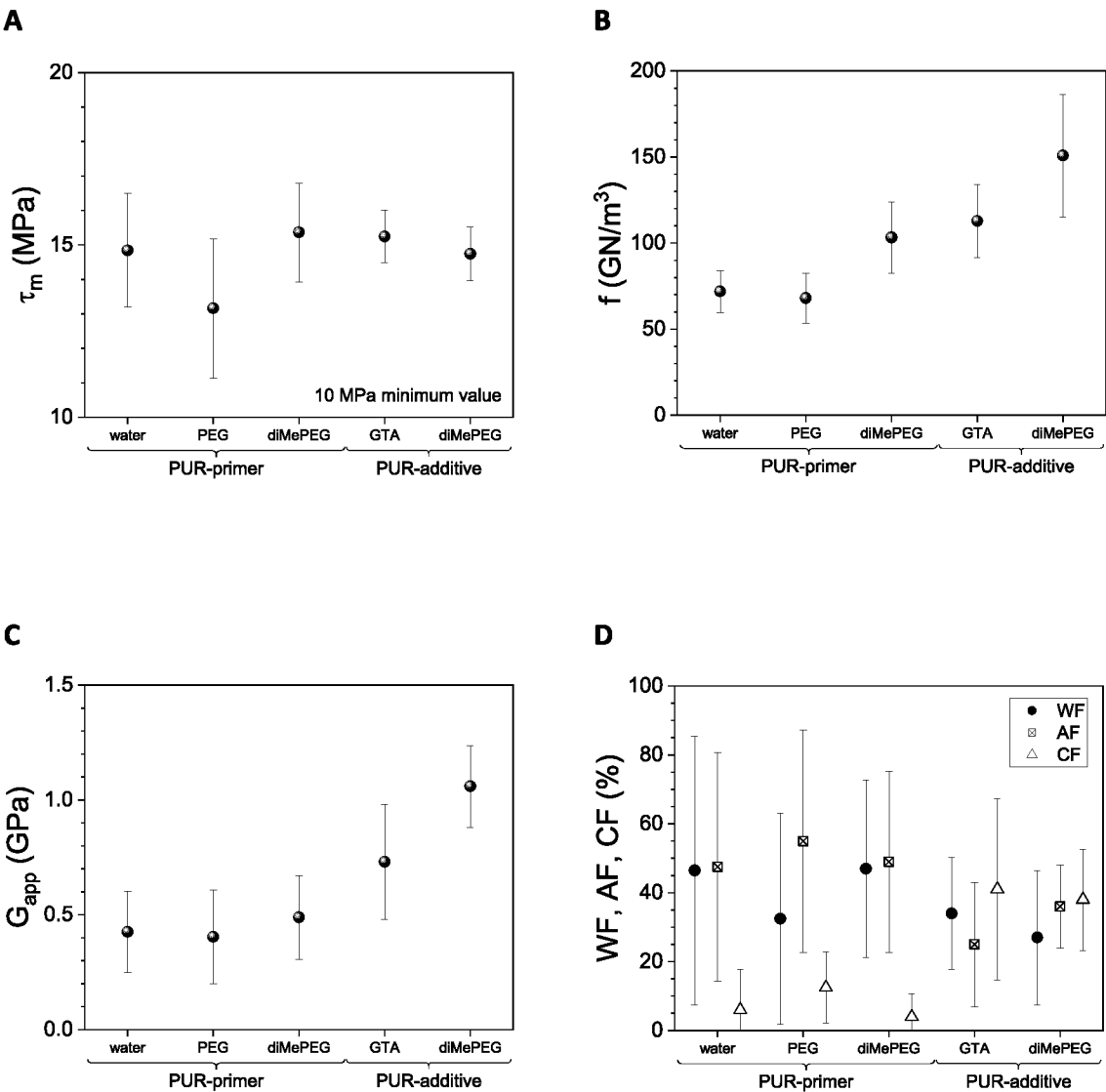


Fig. 3

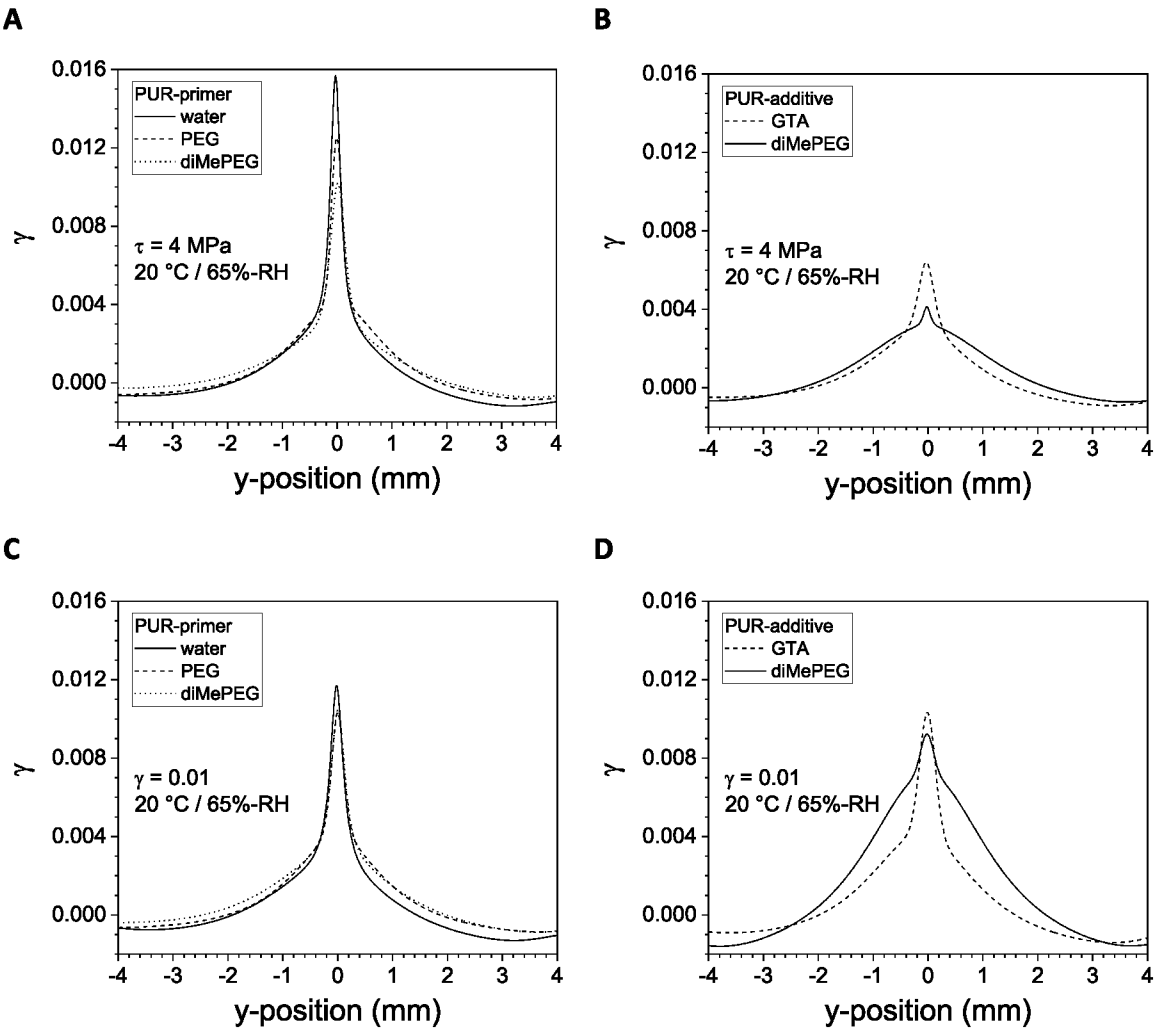


Fig. 4

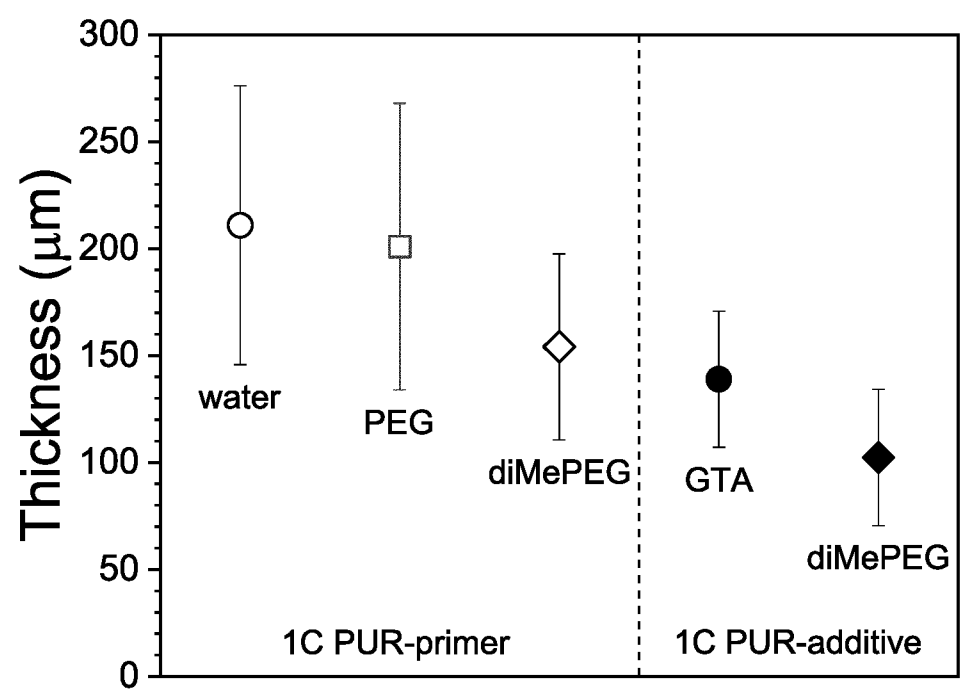


Fig. 5

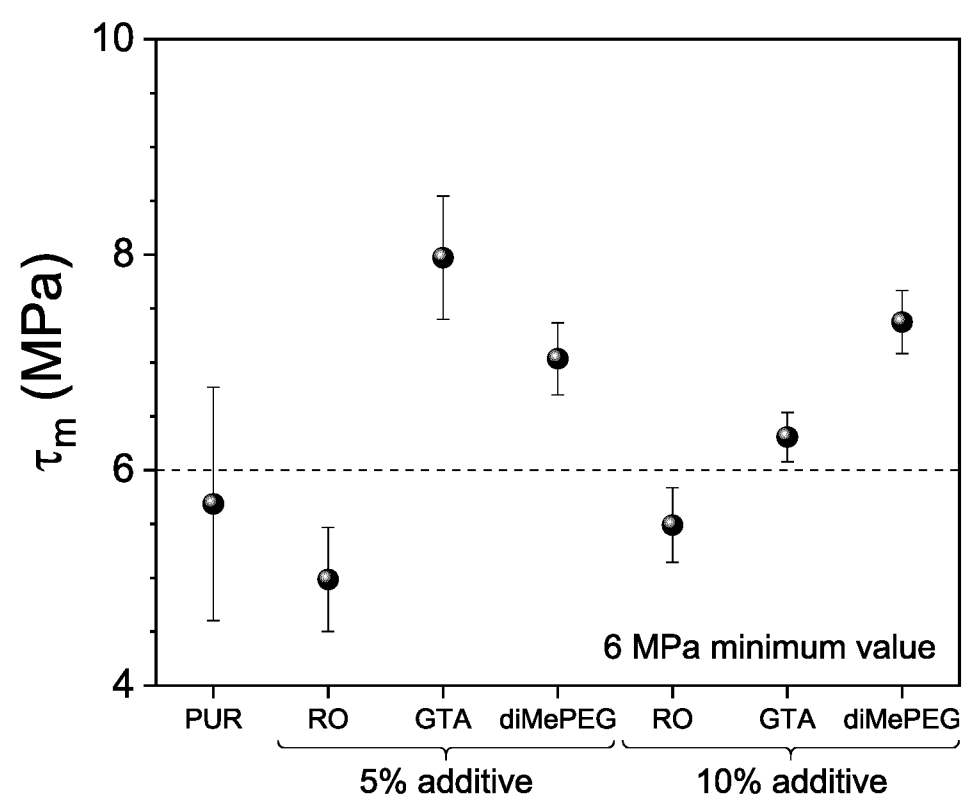


Fig. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2025/071033

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	B32B7/12 C08K5/103 C09J175/04 C08K5/06 C08L71/02	
	B32B21/08 B32B21/13 C08G65/26 C09J5/00	
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) B32B C08J C08K C09J C08L		
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	CN 104 491 922 A (SUZHOU BEC BIOLOGICAL TECHNOLOGY CO LTD) 8 April 2015 (2015-04-08) paragraph [0001]; claims 1-6 paragraph [0015] - paragraph [0049]; examples 1-5; table 1 -----	1 - 15
A	US 2016/168435 A1 (AMEN-CHEN CARLOS [CH] ET AL) 16 June 2016 (2016-06-16) paragraph [0001]; claims 1-20 paragraph [0117] - paragraph [0131] paragraph [0139] - paragraph [0146]; examples; tables 3, 4 paragraph [0004] ----- - / - -	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 "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 24 September 2025		Date of mailing of the international search report 01/10/2025
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Paulus, Florian

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2025/071033

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/274922 A1 (BEATTY RICHARD P [US]) 1 October 2015 (2015-10-01) paragraphs [0010], [0129], [0130]; claims 1-76 paragraph [0200] paragraph [0187] claims 50-53 paragraph [0123] - paragraph [0126] -----	1 - 15
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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 2016168435 A1	16-06-2016	NONE	
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