Removable biobased waterborne Pressure-Sensitive Adhesives containing mixtures of isosorbide methacrylate monomers.

Adrián Badía, Amaia Agirre, María J. Barandiaran, Jose R. Leiza*

POLYMAT, Kimika Aplikatua Saila, Kimika Fakultatea, University of the Basque Country UPV-EHU, Joxe Mari Korta Zentroa, Tolosa Hiribidea 72, 20018 Donostia-San Sebastián, Spain.

Corresponding author: Jose Ramon Leiza, email: jrleiza@ehu.eus

ABSTRACT

Growing environmental concerns are enforcing sustainable recycling processes for glass substrates, especially bottles, where a fast cleaning and minimization of the use of solvents is desired. In this process, labels and adhesives are mostly removed by the addition of harsh reagents, alkaline solutions or high temperature, increasing economic costs and harming the environment. Herein, high performance and biobased waterborne pressure-sensitive adhesives with fast removability in water have been developed using small percentages of isosorbide (derived from glucose) based methacrylate monomers. Formulations containing 2-Octyl acrylate and isobornyl methacrylate and small amounts (1 wt%) of these monomers not only yield stronger adhesive fibrils, but also promote a

removability in water six times faster than that of non-isosorbide based counterparts. This waterborne isosorbide containing PSAs represent an alternative to current PSA formulations towards a more sustainable glass recycling and/or reusing processes.

INTRODUCTION

Waterborne acrylic pressure sensitive adhesives (PSAs) are instantaneous adhesion materials forming part of our daily consuming goods such as tapes and labels, which are often used in glass, PP and PET bottles[1,2]. The PSA labels must adhere strongly to the substrate surface, but in certain applications, after the use of the bottle, debonding of the PSA from substrate is desired (e.g., to reuse and recycle glass bottles). In this context, the cleaning mechanism for removing labels and tapes constitutes a fundamental step during the recycling process, since small amounts of these kind of adhesives may form aggregates in some stages of the process, resulting in an increase of both the operation time and economic costs[3]. Glass bottles are 100% recyclable substrates, which usually have to be cleaned at temperatures of around 85 ºC using basic conditions for removing the labels and adhesives[4]. Therefore, the development of pressure-sensitive adhesives that would easily remove under mild conditions when applied in glass bottles would make this process more sustainable than the current technologies that required high temperatures, aggressive solutions and in some applications solvents or harsh reagents[4–6]. This need has made academia and industry to seek for clean adhesion-switching-off technologies, while ensuring a good performance of the waterborne PSA.

Among the different strategies to achieve these goals, a great variety of water/alkali-soluble tackifiers has been synthesized in the last decades. These are low molar mass polymers mainly composed by ethoxylated alkyl phenols and linear glycols or (meth)acrylate copolymers containing large amounts of carboxyl groups. These resins

promote the removability of the adhesive tape upon immersion in water (cold or hot) and/or alkali conditions[7–14]. However, large amounts (20-70 wt%) are needed and, under high humidity conditions, the tackifier is able to migrate from the adhesive to the adjacent substrate[15–17]. Another alternative to these kind of tackifiers is the use of water-soluble protective colloids such as polyvinyl alcohol, polyvinyl methyl ether, polyethyleneamine, polyethyleneimine, polyvinyl pyrrolidone, polyacrylamide derivatives, hydroxyl ethyl cellulose or carboxymethyl cellulose derivatives[18–23]. These colloids stabilize the polymer particles during the emulsion process and, depending on the performance/water sensitivity ratio desired, different amounts can be used.

Another strategy for developing water-soluble PSAs has been patented by 3M company, combining N-vinyl caprolactam homopolymers (NVC), N-vinyl pyrrolidone copolymers (NVP) and mixtures thereof in presence of ethanol[24,25].

Last but not least, the use of macromonomers based on hydroxyalkyl structures (e.g., HEMA derivatives) has been claimed as well, but a minimun of 15 wt% of these macromonomers is needed and the use of solvents such as ethyl acetate or isopropyl alcohol is required during the polymerization[15,26].

In view of the drawbacks of the approaches presented above, namely, elevated amounts of hygroscopic species, migration possibility and the use of solvents in their synthesis, the development of new strategies that could overcome these issues is gaining more and more interest.

Herein, we propose an isosorbide based methacrylate monomer mixture (the chemical structure is presented in Scheme 1) having a dual functionality: a methacrylate group, susceptible to be polymerized by free radical polymerization and a hydroxyl group giving cohesion and water-affinity. Isosorbide, which comes from the double dehydration of glucose[27], has been widely used and modified in the last few years for thermoset[28–30],

thermoplastic[31], adhesive[32–34] or dental restorative[35] applications. However, to the authors' best knowledge, no reports about the incorporation of isosorbide methacrylate derivatives to produce easily removable waterborne PSAs have been reported.

Scheme 1. Different hard bio-based monomers used in this work and their bio-content value, where the green part belongs to the carbon structure coming from nature resources.

IBOMA (71%)   **PIPEMA (67%)**   **ISOMAraw (60-43%)**
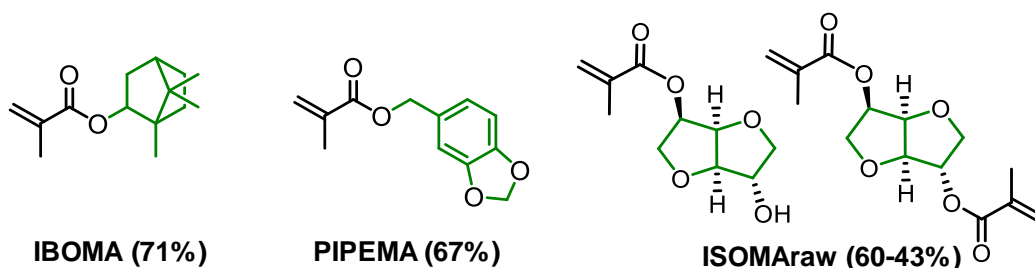
For this purpose, a novel synthetic pathway for the production of a mixture of isosorbide methacrylate derivatives (ISOMAraw) and its purification (to the monomethacrylate isosorbide, ISOMA) was explored. Next, the use of ISOMA and ISOMAraw as the only hard monomer in the formulation of waterborne PSAs was evaluated in terms of adhesive performance and removability. Then, the incorporation of the non-purified mixture (ISOMAraw) and ISOMA as functional monomer in low amounts (1 wt%) was studied. The microstructure (entire molar mass distributions), rheological behavior (storage and loss modulus), adhesion properties (tack, peel resistance, shear resistance and probe tack measurements) and removability by water treatment of PSAs was thoroughly assessed.

These isosorbide methacrylate derivatives can be incorporated in either petroleum-based adhesive formulations or high bio-content ones aiming to reduce the carbon footprint[36,37]. Regarding the last choice, we recently reported the use of 2-Octyl acrylate (2OA) and isobornyl methacrylate (IBOMA) for the synthesis of waterborne PSAs with 70% of bio-content and similar performances than full oil-based commercial PSAs[38], and the use of piperonyl methacrylate for achieving UV-light tunability of the biobased PSA[39]. In this work, we focus on the development of high performance adhesives, based on our previous

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biobased formulations, having the ability to be removed in water at short times and mild conditions. This feature makes them potential candidates for their application in glass bottles aiming at a more sustainable process for the cleaning and reuse of glass bottles.

EXPERIMENTAL SECTION

Materials. Biobased 2-Octyl acrylate (2OA) was kindly supplied by Arkema (France), and both isobornyl methacrylate (Visiomer® Terra IBOMA) and isobornyl acrylate (Visiomer® Terra IBOA) were kindly supplied by Evonik Industries (Essen, Germany). Piperonyl methacrylate (PIPEMA) was synthesized according to the method reported elsewhere[39]. Acrylic and methacrylic acid (AA, MAA), 2-Ethylhexyl thioglycolate (2EHTG) and potassium persulfate (KPS) were purchased from Sigma-Aldrich (Saint-Louis, MO, USA). 2,2´-Azobis(2-methylpropionitrile) (AIBN, initiator), methacrylic anhydride (MAAn, 94% inhibitor 2000 ppm of topanol A), 4-(Dimethylamino)pyridine (DMAP, 99%), magnesium sulfate ($MgSO_4$) and sodium bicarbonate ($NaHCO_3$) were purchased from Sigma-Aldrich (Saint-Louis, MO, USA). Isosorbide (98%), toluene, dichloromethane, hexane and ethyl acetate (99+%) were purchased from Fisher Scientific. Dowfax2A1 (Alkyldiphenyloxide Disulfonate) was kindly provided by Dow Chemical (Midland, Michigan, USA). All reagents were used without further purification.

Synthesis of isosorbide methacrylate mixture (ISOMAraw) and purification to obtain isosorbide 5-methacrylate (ISOMA). The synthesis was carried out following the procedure described by Sadler et al.[29] but increasing the stoichiometry of isosorbide to 1.5 mol. Isosorbide (30 g, 0.205 mol) and DMAP (2.51g, 0.021 mol) were partially dissolved in 250 mL of dichloromethane in a 500 mL round bottom flask equipped with stirrer and dropping funnel. The mixture was stirred at room temperature at a rate of 500 rpm for 20 min. Then it was cooled down to 0ºC (ice-bath) and MAAn (21.1 g, 0.137

mol) was added dropwise for 1 hour. The mixture was stirred overnight. The yellowish solution was quenched with NaHCO$_3$ solution (1M, 100 mL) and then extracted with NaHCO$_3$ solution (1M, 2 x 50 mL), distilled water (3 x 50 mL) and washed with brine (3 x 50 mL). The combined organic layers were dried over MgSO$_4$, filtered and evaporated under reduced pressure yielding in a yellowish oil (ISOMAraw). ISOMAraw is the mixture of both isosorbide methacrylate and dimethacrylate in a molar ratio 8:2. The purification of this mixture by column chromatography (SiO$_2$) using as eluent hexane/ethyl acetate (6:4 v/v) allows the isolation of the monomethacrylate monomer (ISOMA) as a colorless oil. The yields were 56% (ISOMAraw) and 35% (ISOMA), respectively. Scheme 2 shows the reaction pathway to produce isosorbide 5-methacrylate (ISOMA).

Scheme 2. Synthesis of ISOMAraw and ISOMA from isosorbide and MAAn.

Solution homopolymerization of isosorbide 5-methacrylate (ISOMA). (Poly)isosorbide methacrylate (PolyISOMA) was obtained by solution polymerization for the sole purpose of characterizing the Tg of the polymer. For its preparation, 1g of monomer was dissolved in 4g of toluene in a 25 mL volume round bottom flask equipped with a magnetic bar. The reaction was carried out at 70ºC along 5 hours under nitrogen atmosphere using AIBN (1 wbm %) as initiator. Along the reaction, a white insoluble solid in toluene was obtained. The solid was filtered off, washed with toluene and dried under reduced pressure. Note that wbm % makes reference to weight % based on total monomer content.

Table 1. Materials and amounts employed in the synthesis of biobased latexes with ISOMAraw and ISOMA as hard monomers

Materials		wbm %*	Amount (g)
Seed	2OA/IBOA/AA		24.10
Preemulsion composition			
Low Tg monomer	2OA	84	38.96
High Tg monomers	IBOMA PIPEMA ISOMAraw ISOMA	14-15	6.50-6.96
Functional monomers	MAA	1	0.46
Chain transfer agent	2EHTG	0.025	0.0116
Emulsifier	Dowfax2A1	1	1.031
Initiator	KPS	0.25	0.116
Continuous phase	Water		28.60

*weight % based on total monomer content

Emulsion polymerization. 50 wt% solids content (polymer product) acrylic latexes were synthesized by seeded semibatch emulsion polymerization (details are given in the supporting information). Briefly, the reactions were carried out by loading a copolymer seed latex (2OA/IBOA/AA at weight composition of 88/10/2 of 20 wt% solids content and z-average particle size of 121 nm) and a small amount of monomers in the reactor (at 70°C and 200 rpm) and feeding a pre-emulsion of the comonomers for 3 h to reach 50 wt% solids content with a target particle size of 250 nm. Upon finishing the pre-emulsion feeding, the reactor content was post-polymerized for 1 h under the same conditions. The compositions used to synthesize the different PSA latexes are summarized in Table 1 and Table 2. Note that chain transfer agents (CTAs) were used to fine tune crosslinking density and the molar mass distribution of the polymer[38–40].

Characterization. Particle size was analyzed by dynamic light scattering (DLS) and conversion was determined by gravimetry. The gel fraction (or insoluble fraction of the copolymer in THF) was measured by Soxhlet extraction and the molar mass distribution of the whole polymer was determined in THF by asymmetric flow field-flow fractionation (AF4) in combination with a multiangle light scattering (MALS, Dawn Heleos II) and a refractive index detector (RI, Optilab Rex), AF4/MALS/RI. AF4 flow was controlled by Eclipse 3 AF4 Separation System controller (the whole setup from Wyatt Technology). During the separation along the channel in the AF4, the detector-flow was kept constant at 1 mL/min. On the other hand the cross-flow was exponentially decreased from 3 mL/min to 0.05 mL/min except for the Latex A where the cross-flow was decreased in a linear mode from 3 mL/min to 0.05 mL/min. The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC, Q1000, TA Instruments)

Table 2. Materials and amounts employed in the synthesis of biobased latexes using ISOMAraw and ISOMA as functional monomer (1 wt%).

Materials		wbm %*	Amount (g)
Seed	2OA/IBOA/AA		24.10
Preemulsion composition			
Low Tg monomers	2OA	84	38.96
High Tg monomer	IBOMA	14-15	6.50-6.96
Functional monomer	MAA ISOMAraw ISOMA	1	0.46
Chain transfer agent	2EHTG	0.025-0.05	0.0116-0.0232
Emulsifier	Dowfax2A1	1	1.031
Initiator	KPS	0.25	0.116
Continuous phase	Water		28.60

*weight % based on total monomer content

Film preparation. The adhesive films were prepared by casting the latex over a flame-treated polyethylene terephthalate (PET) sheet (29 µm thick) using a gap applicator with reservoir to obtain films of approx. 15 µm thickness. Films were dried protected from dust at 23 °C and 50% humidity for 6h. In the case of probe tack measurements the adhesive film was cast over a glass obtaining a final thickness of 100 µm to avoid the substrate effect.

Evaluating the pressure sensitive adhesives properties. Tests were performed at 23ºC and 50% humidity. Four samples were tested for each formulation and the average values were reported. The peel, loop tack and probe tack tests were performed with a TA.HD Plus Texture Analyzer (Texture Technologies, Hamilton, MA, USA). The holding temperature and shear resistance were tested using SAFT/shear equipment (Cheminstruments, model SS-HT-8). Dynamic mechanical analysis (DMA) was performed with an Anton Paar rheometer using parallel plate geometry. Further information about both the tests and the conditions employed are given in the supporting information.

Removability studies. The studies were performed at room temperature and at 65 ºC in water. For that purpose peel test was carried out using glass as the substrate. The adhesive tapes were attached to the substrate and they were submerged in water. Four samples were tested for each formulation and the average values were reported before and after being submerged in water.

RESULTS AND DISCUSSION

Synthesis of isosorbide methacrylate derivatives (ISOMAraw) and its purification (ISOMA).

Isosorbide is a chiral bicyclic structure presenting two secondary hydroxyl groups at C2 and C5 sites, usually called *exo* and *endo* positions, respectively[27,41]. This chirality together with the V-shaped like structure gives reactivity differences depending on the material used for its functionalization, since *endo*-OH and *exo*-OH have different molecular environments[28,30,42,43]. Although *endo*-OH is more sterically hindered due to the bicyclic conformation, it is also more nucleophilic because of the intramolecular hydrogen bonding with the oxygen of the opposite tetrahydrofuran ring. In addition, numerous studies have been carried out about the reactivity of this alcohol, which can be promoted with the use of catalysts. Thus, it has been claimed the use of electrophilic catalyst based on Na^+ and Li^+, such as NaOH, $NaHCO_3$, CH_3ONa, NaOAc or Li(acac), among others[31]. Moreover, it has been shown that the use of pyridine derivatives, like 4-(Dimethylamino)pyridine, in presence of dichloromethane or tetrahydrofuran promoted the esterification reaction[29,30]. There are few works describing the monomethacrylation of isosorbide in the *endo* position. In the open literature, both a five-step method and an enzymatic method for the synthesis of isosorbide 5-methacrylate have been reported[44,45], while there are patents in which regioisomeric mixtures of monomethacrylates have been synthesized[46,47]. In this work, for the synthesis of isosorbide 5-methacrylate, methacrylic anhydride together with small amounts of a nucleophilic catalyst (4-DMAP) were used in order to promote the electrophilicity of the carbonyl group of the anhydride and thus the attack by the *endo*-alcohol. The use of dichloromethane as solvent could prevent the undesired cleavage of the anhydride yielding methacrylic acid[30].

As described in the experimental section, 1.5 equivalents of this sugar were used in order to minimize the dimethacrylate counterpart, which is produced in the late stages of the reaction by the alcohol at C2 position (*exo*-OH). After this first step a yellowish oil (ISOMAraw) was obtained with a yield of 56%, being the mixture of both

monomethacrylate and dimethacrylate isosorbide in a molar relation 8:2, calculated by

^{1}H NMR. The final yield was low because of the water solubility of ISOMAraw, which

made difficult its extraction during the working up process. This product can be used as

produced without further purification (as a mixture of monomethacrylate and

dimethacrylate isosorbide monomers) or can be purified by column chromatography

using a mixture of hexane and ethyl acetate (6:4) as eluent. Figure 1 (a) shows the [1]H

NMR spectrum of ISOMAraw in chloroform-d_1, observing the monomethacrylate

isosorbide as major product. Proof of this is the multiplet at 4.3 ppm corresponding to the

proton at the position C2 of the bicyclic, this is the one next to the free OH group.
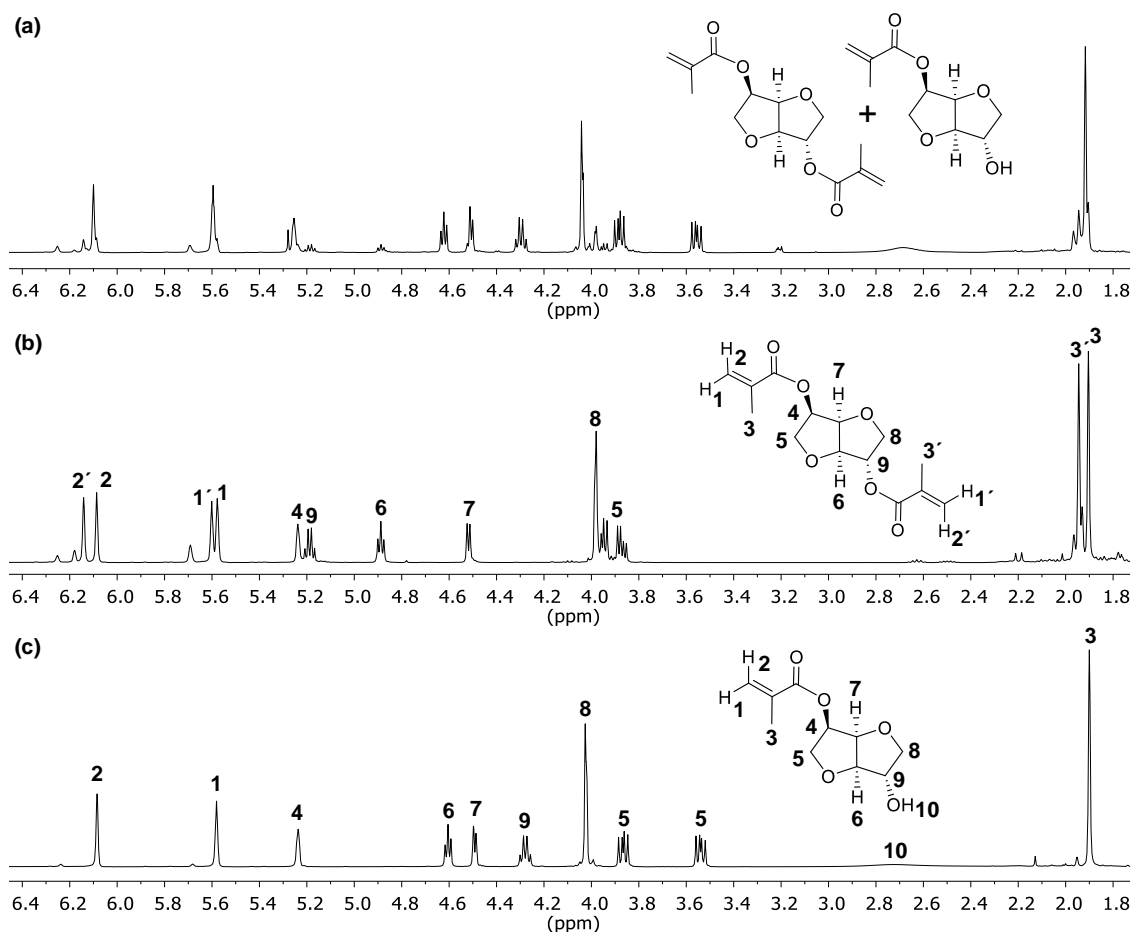
Figure 1. ^{1}H NMR spectra in chloroform-d_1 of (a) ISOMAraw, (b) Isosorbide dimethacrylate and (c) Isosorbide 5-methacrylate. Note that the spectra are showed in order of the chromatographic column elution time. The chemical shifts of both isosorbide

dimethacrylate and isosorbide 5-methacrylate are listed in Figure S1 of the supporting information.

The subsequent purification allowed to separate the dimethacrylate product (Figure 1.b) and then the monomethacrylate one (Figure 1.c) as a colorless oil (ISOMA) with a final yield of 35% and a bio-content of 60%. However, small signals were detected around 5.7 and 6.3 ppm in both fractions, corresponding to the methacrylate units chemical shift. This is indicative of the formation, in a small quantity, of the *exo*-methacrylate (Isosorbide 2-methacrylate) which has a lower presence (<1%) in the final product.

Solution homopolymerization of isosorbide 5-methacrylate (ISOMA)

Solution homopolymerization of the biobased monomer isosorbide 5-methacrylate was performed using toluene as solvent and AIBN as thermal initiator. A white crystalline solid was obtained (polyISOMA) as the reaction advanced as consequence of the insolubility of the homopolymer in the reaction medium, reaching a conversion higher than 99% (calculated by ^{1}H NMR integration).

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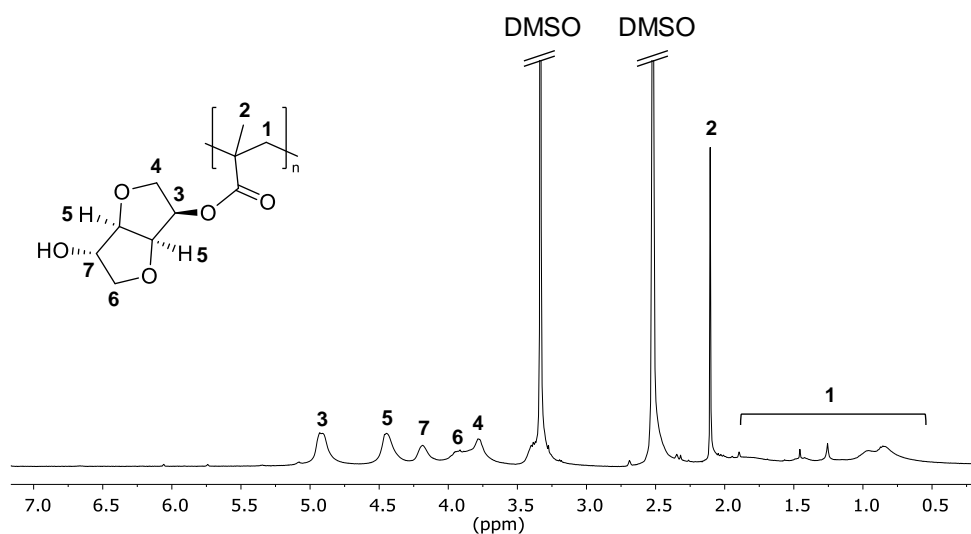
Figure 2. ^{1}H NMR spectra in DMSO-d_6 of (Poly)isosorbide 5-methacrylate (PolyISOMA).

Differential scanning calorimetry provided the thermal transition of polyISOMA (See Figure S2), which presents a glass transition temperature around 80 ºC because of its non-bulky and V-shaped like bicyclic structure, which allows a higher free volume and hence lower Tg than other rigid aromatic substituents (e.g., polystyrene, polyphenylmethacrylate). Nonetheless, the Tg is still high enough as to play the role of hard monomer in PSA formulations. It is worth mentioning that a Tg of 140 ºC has been reported for the homopolymer of isosorbide dimethacrylate[30]. This value is related with both the absence of flexibility of the molecule and the high crosslinking density limiting the molecular motion[48].

Waterborne PSAs using ISOMAraw and ISOMA as hard monomer: Comparison with IBOMA and PIPEMA

Aiming to investigate the effect of the hard monomer nature on the performance of the waterborne biobased PSAs, a comparison study of PSAs produced from latex having the general formulation: 2OA:*Hard monomer*:MAA + CTA (84:15:1 + 0.025), where the hard monomer is IBOMA, PIPEMA or ISOMAraw, was carried out. Notably a formulation with 15 wt% of ISOMA (isosorbide 5-methacrylate) was also attempted, but the system started to be unstable at 30-60 min of reaction (aggregation of particles) yielding a large amount of coagulum at the end of the process (see Figure S3). A more detailed description of this section and explanation of the unsuccessful polymerization when ISOMA monomer was used in the formulation can be found in the Supporting Information. In addition, a summary and characteristics of the PSA latexes as well as of PSA tapes containing different hard monomers can be found in Table S1 and Table S2, respectively.

Briefly, the use of ISOMAraw led to an adhesive material with poor tackiness, not being able to form fibrils during the debonding process. The explanation for such solid-like behavior is the high crosslinking density because of the presence of dimethacrylate isosorbide monomer in the formulation, which reduced the work of adhesion increasing both holding temperature and shear resistance.

It is well known that the hydrophilicity of a monomer can promote its incorporation on the surface of the polymer particles in emulsion polymerization processes[49,50]. In this vein, the free hydroxyl group of the isosorbide derivative monomer (ISOMA) could allow its incorporation on the surface of the growing particles. This strategy could improve the adhesion properties of the tape on glass substrates as well as its removability in water. Scheme 3 illustrates this process, in which part of the OH groups of the particle would be located at the air-adhesive interface. Those free hydroxyl groups may interact with silanol groups (in the glass surface) via hydrogen bonding improving mechanical properties, but it could also increase the sensitivity to water (interaction with water could cleavage this non-covalent bond).

Scheme 3. Disposition of the OH groups of the particles surface after the drying process and their interaction with the glass substrate.
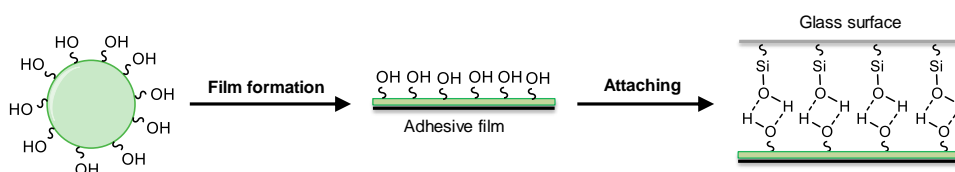
In order to evaluate the sensitivity to water, removability studies of the PSA tapes attached to glass substrates were carried out by measuring the evolution of the 180° peel strength before and after the water treatment (see Figure 3). This experiment revealed that PSA tapes containing ISOMAraw reached a complete removability in water after 20 min of immersion at room temperature. This aspect is of special interest for adhesive

formulations targeted for glass bottles labels, since short times, low energy consumption and the lack of solvents are desired during their cleaning process.
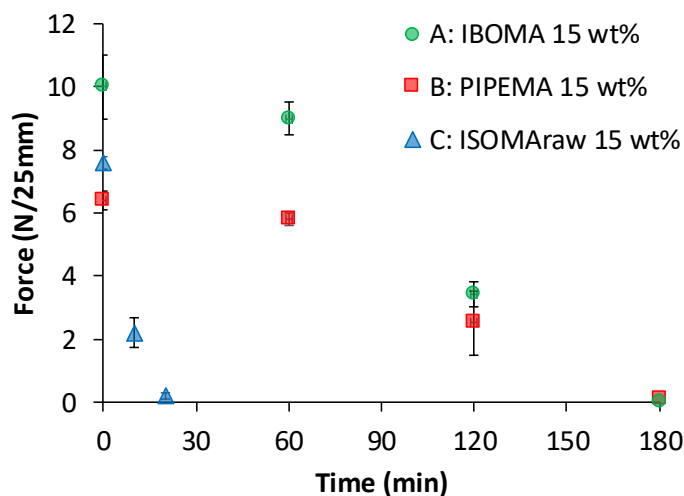
Figure 3. Evaluation of 180º peel strength at different times of water treatment at room temperature on glass of PSA tapes with the formulation 2OA: **Hard monomer**: MAA + CTA (88:**15**:1 + 0.025 wbm%).

Incorporation of ISOMAraw/ISOMA as functional monomer in waterborne PSAs with IBOMA as hard monomer.

In view of the effects of ISOMA (monomethacrylate) and ISOMAraw (mixture of mono

Table 3. Properties of the PSA latexes containing 2OA:IBOMA as main formulation, and ISOMA and ISOMAraw as functional monomer.

PSA	Composition (%wt monomers)	dp (nm)	Gel (%)†	Tg (°C)	Bio (%)
	2OA:IBOMA: ISOMAraw:MAA				
A*	84:15:0:1	230	59 ± 0.4	-26	72
A.1*	84:14:1:1	236	65 ± 0.5	-27	72
A.2**	84:14:1:1	235	55 ± 1	-27	72
	2OA:IBOMA: ISOMA:MAA				
A.3**	84:14:1:1	235	50 ± 1	-29	72

* and ** make reference to 0.025 wbm% and 0.05 wbm% of 2EHTG, respectively.

† The fraction of the copolymer that does not dissolve in THF after 24 h of soxhlet extraction.

and dimethacrylate) on the polymerization and the performance of the adhesives and its

removability in water, it was considered to use them in the formulation of waterborne adhesives at lower percentages, namely, as functional monomer rather than as hard monomer. Thus, ISOMAraw or ISOMA monomers were incorporated into latex formulations (see Table 2 and Table 3) aiming to enhance both the removability of the adhesive tapes from glass substrate and increasing their performance. In order to control the final insoluble polymer fraction the amount of CTA (2EHTG) was adjusted in the PSA compositions. Table 3 summarizes the latexes synthesized for this purpose as well as their main properties including particle size (dp), gel content (measured by soxhlet extraction) and the glass transition temperature.

Figure 4 presents the molar mass distributions determined using AF4/MALS/RI. As can be appreciated, bimodal molar mass distributions were obtained with the high molar mass peak centred at around 10^9 Da and the low molar mass peak at around 10^5-10^6 Da. The incorporation of ISOMAraw in formulation **A.1**, using the same amount of CTA than the reference formulation **A**, increased the insoluble polymer fraction (gel polymer) and this was more crosslinked as reflected in the MMD that showed a slight shift of the high molar mass mode. At the same time the low molar mass mode shifts to lower masses because of the preferential incorporation of the high molar masses to the gel polymer (the high molar mass mode). When the CTA amount was increased (formulation **A.2**) the gel content decreased and the high molar mass peak slightly shifted to lower values, indicating a less crosslinked polymer network due to the reduced efficiency of the isosorbide dimethacrylate crosslinker at higher chain transfer agent concentrations. Furthermore, the low molar mass mode was shifted to even lower values than formulation **A.1** due to the combined effect of less crosslinking reactions and shorter kinetic chain lengths.
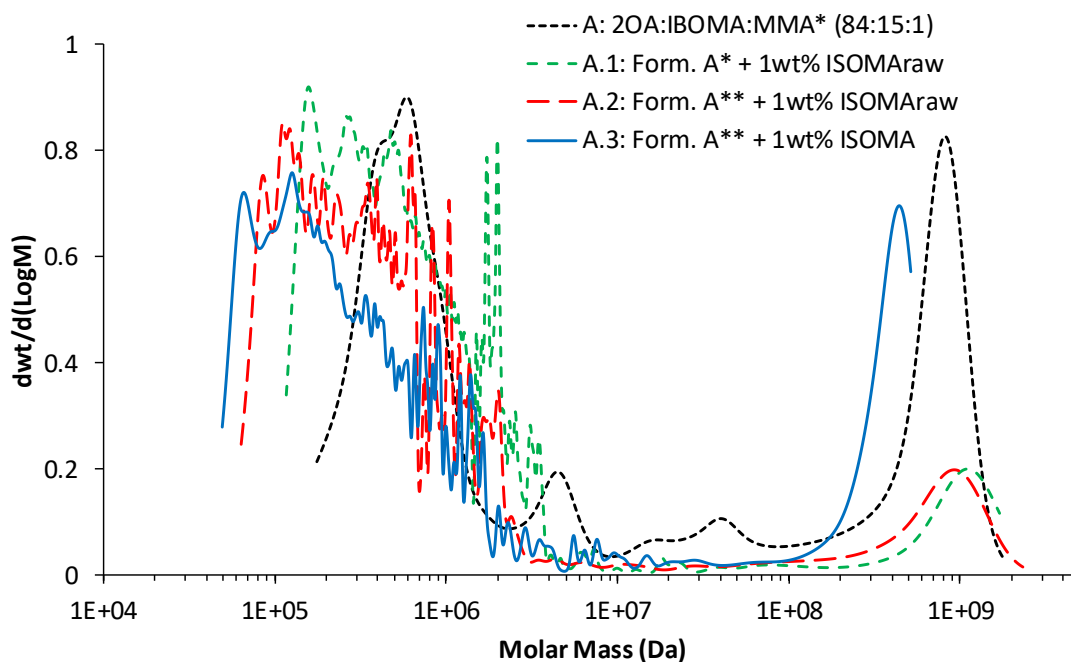
Figure 4. Molar mass distributions measured by AF4/MALS/RI for the four latexes of this section. Note that Formulation A makes reference to 2OA:IBOMA:MAA (84:14:1). The substitution of ISOMAraw by ISOMA, namely, the elimination of isosorbide dimethacrylate in formulation **A.3** led to the lowest gel content among all the formulations. Both, the high molar mass and low molar mass modes of the MMD distribution were shifted to lower molar masses in good agreement with the lack of dimethacrylate monomer and the highest concentration of CTA used.

Dynamic rheological experiments were carried out aiming to correlate the microstructure of the adhesives with their viscoelastic properties. Figure 5 shows the variation of storage and loss modulus and the damping factor with the frequency at 23 ℃. All formulations presented storage modulus values below 0.1 MPa and a value of $\tan\delta/G' > 5$ MPa^{-1}, which have been recommended for pressure-sensitive adhesives to have good contact in a short time[51,52].

It can be observed that formulation **A.1** showed the lowest value of both G′ and G′′ at the debonding frequency (1 Hz). The result for the loss modulus was because of the higher

gel content (higher crosslinking density of the high molar mass fraction), which reduced the viscous behavior of the material. Nonetheless, the elastic component of the material (related with G´) is not consistent with this microstructure. This could be related with the presence of chains with lower molar masses (see Figure 4, green line), which reduced the capability for storing energy, but increased the dissipation of energy (tanδ/G´ = 8.7). Higher moduli (G' and G'') values were observed for formulations **A.2** and **A.3**, not showing relevant differences regarding the viscous component. It seems that the enhancement of the chain mobility, because of the higher amount of CTA, promotes supramolecular interactions (hydrogen bonding between isosorbide moieties), which contribute to the storage (elastic component), but also to the dissipation (viscous component) of energy. The increase in the solid-like behavior was also reflected in the energy dissipation capability at the interphase adhesive-substrate (tanδ/G´), whose value drop down for formulations **A.2** (tanδ/G´ = 7.1) and **A.3** (tanδ/G´ = 7.7).
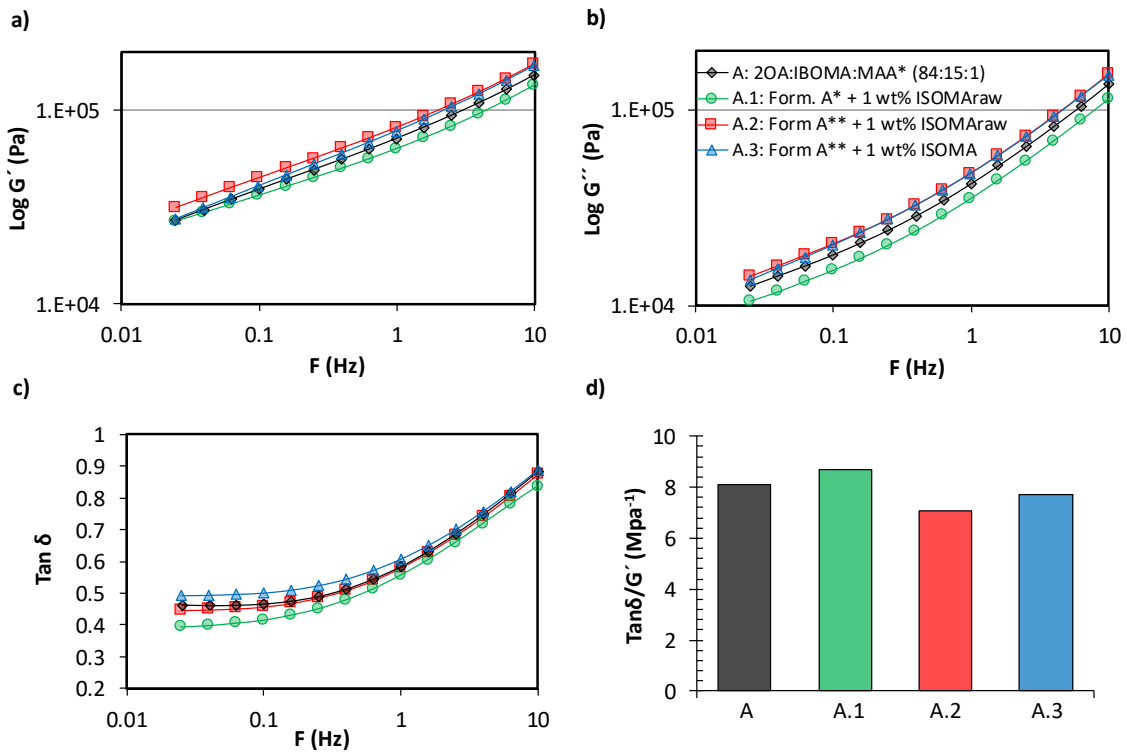
Figure 5. (a) Storage modulus (G′), (b) loss modulus (G″), c) dynamic modulus (tanδ) and (d) tanδ/G′ for 2OA:IBOMA formulations containing ISOMA or ISOMAraw as functional monomer. Measurements made at 23 ºC and 1 Hz.

The adhesive properties of these four latexes are shown in Table 4. The presence of ISOMAraw in formulation **A.1** reduced a little bit the peel strength without affecting

**Table 4.** Adhesive properties of the PSA tapes containing 2OA:IBOMA as main formulation.

PSA	Composition	Peel (N/25mm)	Loop tack (N/25mm)	WA (J/m^2)	Shear resistance (min)	SAFT (°C)
	2OA:IBOMA: ISOMAraw:MAA					
A*	84:15:0:1	6.7 ± 0.7	7.7 ± 0.3	139 ± 14	8640	133 ± 1
A.1*	84:14:1:1	5.5 ± 0.4	7.2 ± 0.2	128 ± 10	1530 ± 60	157 ± 5
A.2**	84:14:1:1	8.9 ± 0.5	8.3 ± 0.3	144 ± 10	1110 ± 60	130 ± 5
	2OA:IBOMA: ISOMA:MAA					
A.3**	84:14:1:1	7.2 ± 0.6	9.4 ± 0.5	176 ± 20	510 ± 3	120 ± 2

* and ** makes reference to 0.025 wbm% and 0.05 wbm% of 2EHTG, respectively.

tackiness and work of adhesion. This lightly crosslinked polymer network resulted in a higher holding temperature, but lower shear resistance, likely because low molar mass polymer chains reduced the cohesiveness of the adhesive along the time. The decrease of the gel content in formulation **A.2** enhanced the polymer chains mobility, namely, the liquid-like behavior, improving both peel strength and loop tack, but affecting shear resistance and SAFT. Formulation **A.3** used ISOMA and as shown in Figure 4 (blue line) the high molar mass peak shifted to lower values and gel content decreased. This was translated into an increase of the instantaneous adhesion as well as the work of adhesion. However, due to reduction in the cohesiveness both peel strength and shear resistance were decreased. It is noteworthy that an adhesive failure was observed for all the formulations.

Figure 6 shows the probe tack curves for these formulations. At first view, the incorporation of ISOMAraw provided stronger but also more flexible adhesive fibrils. Regarding this, the presence of a substantial fraction of the polymer (the high molar mass mode) forming a covalent crosslinked network enhanced the solid-like behaviour, but the low molar mass fraction also promoted the motion of the polymer chains, yielding stiff and flexible fibers. As consequence, a broader stress peak at lower strain values followed by a longer fibrillation plateau at higher stress was observed for formulation **A.1**. There is a reduction of the rate at which the cracks, formed by the cavitation process, propagate to the interface resulting in a greater elongation of the fibrils formed[53]. Formulation **A.2** showed even a longer elongation at break with a little reduction of the plateau height because of the greater viscous behaviour. The decrease in tanδ/G′ value is in agreement with the broader initial stress peak in the probe tack curve, which is related with a greater contribution of G′.

The use of ISOMA in formulation **A.3** yielded an interesting shape of the probe tack curve. The stress plateau suggests a reinforcement of the adhesive fibrils during the dissipation of energy, showing a slight shoulder which breaks around 420% of strain. This reinforcement could be attributed to supramolecular interactions (hydrogen bonding interactions) which promote the ability for storing energy up to certain stress during the elongation. Above this limiting stress the interaction is broken and hence this results in a sudden release of the stored energy. In this context, there is an interfacial contribution of supramolecular bonds among the polymer chains, namely, the motions within the walls of the cavities[54,55]. Moreover, the less-constricted polymeric structure facilitates motion promoting hydrogen bonding and hence the alignment of the polymer chains. This is in accordance with the rheological results, since the hydrogen bonding interactions benefit the solid-like behavior, namely, the storage modulus (G′), affecting to the tanδ/G′ value.
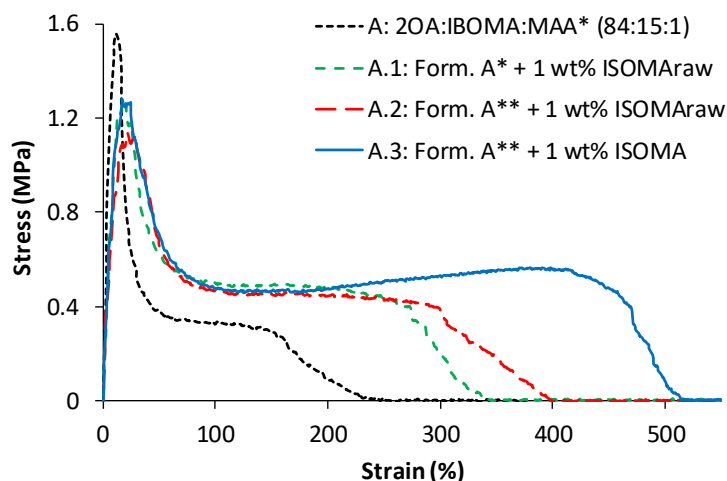
Figure 6. Probe tack tests for 2OA:IBOMA formulations.

Notably, the adhesive performance of these PSA compositions having a 72% of biobased content excels to those commercial ones which are fully-petroleum based (see comparison in the Supporting Information). The use of low amounts of either ISOMAraw or ISOMA not only improved the fibrils flexibility, but also their strength, contributing positively to the added value of the material.

In order to know the impact of small fractions of this sugar derivative monomer in the water sensitivity of the adhesive tapes, removability studies were performed by assessing the peel strength of adhesive films adhered on glass and immersed in water over time (at room temperature as well as at 65 °C). The results are shown in Figure 7. The incorporation of only 1 wt% of ISOMAraw in the case of formulations **A.1** and **A.2** promoted their complete detachment after 40 min without letting any noticeable adhesive residue on the glass surface. On the other hand, the use of ISOMA in formulation **A.3** increased the peel strength on the glass surface before the water treatment and promoted an even faster detachment, reaching the complete removal in almost 30 min. Finally, Figure 7b shows that the water treatment at 65 °C sped up the process, achieving complete removal of the adhesive tapes in 10 min for those formulations containing the isosorbide derivative monomer.
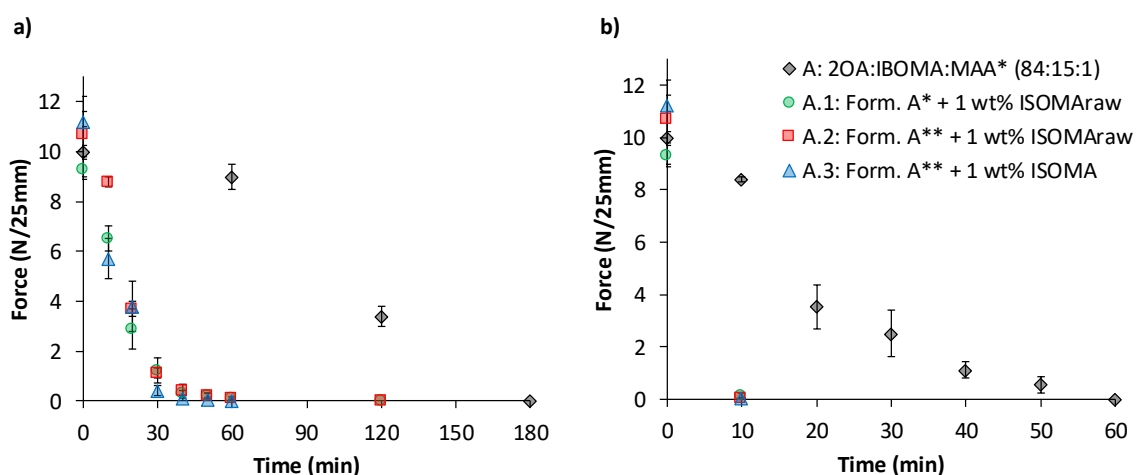
Figure 7. Evaluation of 180º peel strength at different times of water treatment at room temperature (a) and at 65 ºC (b) on glass for PSA tapes containing 2OA:IBOMA as main formulation and ISOMA or ISOMAraw as functional monomer.

To sum up, it is remarkable the effect that small amounts (1wt%) of these isosorbide monomers (either ISOMAraw or ISOMA) have both in the adhesive performance of the PSAs (see supporting information for a comparison with oil-based commercial-like formulations) and in the removability from glass substrates in mild conditions (water). The use of this high performance and easily removable adhesives in glass bottles can make the reuse and recycle of glass bottles a substantially more sustainable process by reducing energy consumption and the use harsh solvents.

CONCLUSIONS

Environmental concerns are promoting more and more sustainable technologies regarding the recycling processes of a wide range of materials. The removability of the PSA tapes and labels from glass bottles represents an important step during the glass cleaning, being achieved by the use of solvents or alkali solutions at high temperatures. In this context, the manufacturing of waterborne PSAs with potential performance and easy removal capability constitutes an important improvement for the sustainability of the recycling of such bottles (lower energy and solvent consumption). In this work, the

synthesis of a dual functional monomer derived from isosorbide, more specifically isosorbide dimethacrylate, isosorbide 5-methacrylate and mixtures thereof, and its incorporation into biobased PSA formulations was investigated. It was found that the incorporation of ISOMAraw in waterborne PSAs by emulsion polymerization (at 14 wt%) yielded a slightly crosslinked polymer network having poorer adhesion properties than formulations with other hard monomers (IBOMA or PIPEMA), but promoting the removability of the adhesive tape from glass in water in substantially shorter times (~20 min). Nonetheless, small amounts (1 wt%) of ISOMAraw/ISOMA in PSA formulations containing IBOMA as hard monomer and 2OA as soft monomer enhanced both the flexibility and the cohesiveness of the adhesive fibrils, namely, the adhesion performance. Even more interesting was the fact that those small amounts of ISOMAraw/ISOMA promoted the complete removability of the PSA tapes in water in less than 40 min at room temperature, being 4 times faster at 65 ℃. These results shed light about the development of novel waterborne PSA formulations having up to 72% of biocontent and containing low percentages of an isosorbide methacrylate monomer which enhances the adhesive performance and provides a positive impact on the glass bottles cleaning, minimizing times and energy consumption and avoiding the use of solvents.

Supporting information. Seed preparation and Synthesis of the desired latexes; characterization; ^{1}H NMR of isosorbide dimethacrylate and isosorbide 5-methacrylate monomer; DSC of polyISOMA; Waterborne PSAs using ISOMAraw and ISOMA as hard

monomer and their comparison with IBOMA and PIPEMA; comparison of adhesive performance of series **A** and an oil-based commercial pressure-sensitive adhesive.

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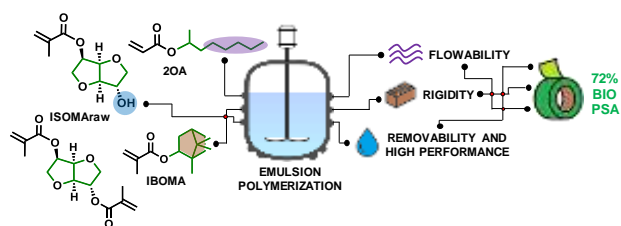
Biobased waterborne pressure sensitive adhesives (based on 2OA, IBOMA and ISOMAraw/ISOMA biobased monomers) produced by a sustainable emulsion polymerization process present high adhesive performance and removability in water.