



Easy removable and UV tunable biobased waterborne pressure sensitive adhesives

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ABSTRACT

Herein, high performance and biobased waterborne pressure sensitive adhesives having the ability to be removed in water at short times and being tunable upon UV-light have been developed. The combination of two functional monomers, namely, an isosorbide derivative monomer and piperonyl methacrylate in PSA formulations containing 2-octyl acrylate (2OA) as main monomer provided strong and extensible adhesive films. Besides, the adhesive films can be post-treated by UV-irradiation enhancing cohesion of the adhesives, via crosslinking reactions between benzodioxole groups, hence fine tuning their performance. The presence of low amounts of the sugar-based derivative monomer (1 wt%) promoted the removability in water of the PSA tapes, which was kept after the UV-light curing.

1. Introduction

In recent years, fluctuation of petroleum prices, consumer demands, environmental concerns and strict regulations about the greenhouse gas emissions (particularly CO₂) have pushed up our society towards the development of sustainable materials [1]. In this context, there is an interest for replacing current petroleum-based materials by renewable feedstock together with the use of “green technologies”, specifically emulsion polymerization, aiming to reduce the carbon footprint and avoid the use of solvents during the process [2]. This strategy is implemented more and more in the production of daily consumer goods such as adhesives and coatings, this is, polymers having a prominent area of interest for industry and academia, which seek for new renewable building blocks for their formulations [3].

Waterborne acrylic pressure sensitive adhesives are environmentally friendly materials which can strongly adhere to solid surfaces upon light pressure and short contact times [4,5]. These instantaneous adhesion materials, widely used as tapes and labels for packaging products and glass or plastic bottles, have undergone an extensive research over the past years in order to increase the bio-content of their formulations. Concerning this, Bunker et al. [6] [7] designed waterborne PSA copolymers with biobased acrylated methyl oleate together with oil-based methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA). Pu et al. [8] reported the synthesis of a biobased

macromonomer coming from HEMA, lactide and ϵ -caprolactone and its copolymerization together with *n*-butyl acrylate to produce PSAs with 34% biomass content. Moreno et al. [9,10] carried out the polymerization of the methacrylated oleic acid (MOA) monomer and its copolymerization with α -methylene- γ -butyrolactone to produce waterborne dispersions with potential uses in the PSAs field. More recently, Noppalit et al. [11] synthesized and copolymerized tetrahydrogeraniol acrylate (THGA) and cyclademol acrylate (CDMA), but adhesive performance of the films was poor. Sugar-based acrylate macromonomers have also been copolymerized with conventional acrylates in an emulsion process to obtain repulpable PSAs [12]. Waterborne PSAs with bio-contents up to 72% containing the commercial biobased monomers 2-octyl acrylate (2OA) and isobornyl methacrylate (IBOMA) were deeply explored by our research group. However, shorter fibrillation plateaus and, thus, lower adhesion energies were obtained in comparison with a commercial-like petroleum-based formulation [13]. Recently, Molina-Gutierrez et al. [14] explored the synthesis of waterborne PSAs using eugenol-derived methacrylates as hard monomer (in total or partial substitution of methyl methacrylate) together with petroleum based butyl acrylate and methacrylic acid. They found that the performance of the PSAs with the eugenol derivative methacrylate were better than a commercial Scotch Magic® tape, but slightly worse than the full petroleum counterpart.

At this point it is worth to mention that since the petroleum price is

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still low and the market value of the adhesives sector is high, renewable monomers must guarantee not only the “green label” concept, but also offer additional functionalities. Therefore, the performance of the bio-based material is expected to overcome or compete with the ones coming from petroleum-based counterparts by providing extra benefits [15]. The fine tuning of the adhesive microstructure by physical stimuli (temperature, electricity or UV-light) or the easy debonding/degradation under mild conditions are important functionalities aimed for the industrial applications. Regarding this, we reported that the incorporation of piperonyl methacrylate (PIPEMA), a benzodioxole derivative monomer, into waterborne bio-based PSA formulations allowed an easy control of the crosslinking degree of the polymer network with the UV-light irradiation time [16]. Additionally, we recently found that small amounts of isorborne dimethacrylate, isorborne 5-methacrylate (ISOMA) and mixtures thereof (ISOMArAw) enhanced both the flexibility and the cohesiveness of the adhesive fibrils and, more interestingly, promoted the removability in water of the PSA tapes at mild conditions and short times [17,18]. This feature results of special interest during the washing processes of reusable glass bottles, which usually need hours for a complete and clean removal of the label, the use of basic conditions at high temperatures ($\approx 85^\circ\text{C}$) or even the presence of solvents and harsh reagents.

In this work, and taking into account our previous bio-based formulations, we focus on the combination of piperonyl methacrylate together with small percentages of such isorborne methacrylate monomers. Therefore, the goal is to produce high performance and UV-light tunable waterborne PSAs having the capability to be removed in water in an efficient way. For this purpose, the incorporation of the non-purified mixture (ISOMArAw) and ISOMA as functional monomer in low amounts (1 wt%) was studied in PSA formulations containing 2OA and PIPEMA as soft and hard monomers, respectively. The microstructure, rheological behavior, adhesion properties before and after curing by UV-light and removability by water treatment of PSAs was thoroughly assessed. Scheme 1 shows the main bio-based monomers used in this work together with their bio-content.

2. Experimental

Materials. Bio-based 2-octyl acrylate (2OA) and isobornyl acrylate (Visiomer® Terra IBOA) were kindly supplied by Arkema (France) and Evonik Industries (Essen, Germany), respectively. Piperonyl methacrylate (PIPEMA) and isorborne methacrylate monomers (ISOMArAw/ISOMA) were synthesized according to the method reported elsewhere [16,17]. It is worth to mention that ISOMArAw is the mixture of both monomethacrylate and dimethacrylate isorborne in a molar relation 4:1. Acrylic and methacrylic acid (AA, MAA), 2-ethylhexyl thioglycolate (2EHTG), 1-butanethiol (BuSH) and potassium persulfate (KPS) were purchased from Sigma-Aldrich (Saint-Louis, MO, USA). Dowfax2A1 (alkyldiphenyloxide disulfonate) was kindly provided by Dow Chemical (Midland, Michigan, USA). All reagents were used without further purification.

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. Note that chain transfer agents (CTAs) were used to fine tune crosslinking density and the molar mass distribution of the polymer [13,16,19].

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 (490 μm width) 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. The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC, Q1000, TA Instruments).

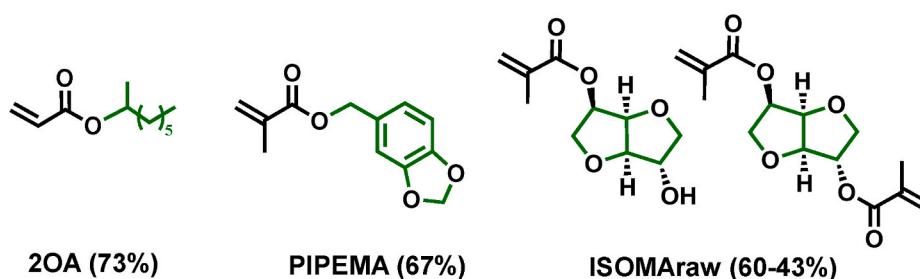
Film preparation. The adhesive films were prepared by casting the latex over a flame-treated polyethylene terephthalate (PET) sheet (29 μm thick) using a gap applicator with reservoir to obtain films of approx. 15 μm thickness. Films were dried protected from dust at 23°C and 50% humidity for 6 h. In 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. The thickness of the adhesive films was measured

Table 1

Materials and amounts employed in the synthesis of bio-based latexes containing PIPEMA as hard monomer and ISOMArAw and ISOMA as functional monomer (1 wt%).

Materials		wbm % ^a	Amount (g)
Seed	2OA/IBOA/AA		24.10
Preemulsion composition			
Low Tg monomers	2OA	84	38.96
High Tg monomer	PIPEMA	14–15	6.50–6.96
Functional monomer	MAA	1	0.46
	ISOMArAw		
	ISOMA		
Chain transfer agent	2EHTG	0.025–0.05	0.0116–0.0232
	1BuSH	0.075	0.0348
Emulsifier	Dowfax2A1	1	1.031
Initiator	KPS	0.25	0.116
Continuous phase	Water		28.60

^a Weight % based on total monomer content.



Scheme 1. Main 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.

with a micrometer.

Evaluating the pressure sensitive adhesives properties. Tests were performed at 23 °C and 50% humidity. Four samples were tested for each formulation and the average values were reported. In the case of probe tack test, ten measurements of each formulation were carried out and the average curve was plotted. The 180° 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. UV-light curing of the PSA films was performed by a UV-light source (Compact 4-Watt UV Lamp, 6 W tube lamp of shortwave 254 nm) at room temperature in a dark chamber with a distance of 10 cm between the irradiation source and the film. 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 °C in deionized water (Mili Q quality). For that purpose the standard 180° peel test (described in the supporting information) was carried out using glass as the substrate. The adhesive tapes were attached to the substrate and they were submerged in water. After the immersion time the panels were carefully dried with absorbent paper and 180° peel test was performed. Four samples were tested for each formulation and the average values were reported before and after being submerged in water.

Swelling degree. The swelling degree evolution of the polymer films at different UV-irradiation times was measured using tetrahydrofuran (THF) as solvent. After the irradiation, the polymer film was submerged in a closed vial containing THF for 24 h. Then, the swollen film was carefully dried from the THF excess and weighed. The swelling degree was calculated as follows:

$$\text{Swelling degree} = \frac{w_s - w_p}{w_p} \quad (1)$$

where w_s is the weight of the swollen polymer sample (polymer + solvent) and w_p is the weight of the dry polymer sample (polymer film before the immersion).

3. Results and discussion

Table 2 summarizes the latexes synthesized as well as their main properties including particle size (d_p), gel content (measured by soxhlet extraction) and the glass transition temperature.

Fig. 1 shows the molar mass distributions determined using AF4/MALS/RI. As can be appreciated, bimodal molar mass distributions were obtained for all the formulations with the high molar mass in the range 10^8 – 10^9 Da and the low molar mass peak at around 10^5 – $5 \cdot 10^6$ Da. The addition of ISOMArAw in formulation A.1 at the same CTA concentration than formulation A slightly shifted the high molar mass peak at higher values (green line) and broadened the molar mass of the low mode as compared with formulation A.

The gel content, in agreement with this trend, increased to $58 \pm 0.1\%$, being indicative of a more crosslinked polymer network. The increase of CTA for the same concentration of ISOMArAw (formulation A.2) decreased the molar mass of the high molar mass mode (making it smaller than for the pure 2OA/PIPEMA) due to the competition of the chain transfer to CTA with the propagation to pendant double bonds coming from the isosorbide dimethacrylate crosslinker. In addition, the low molar mass mode also shifted to slightly lower values because of the combined effect of less crosslinking reactions and shorter kinetic chain length.

The substitution of ISOMArAw by ISOMA in formulation A.3 affected the MMD of the latex in a similar manner, both, the high molar mass mode and the low molar mass mode shifted to lower molar masses in agreement with the substantially lower insoluble polymer measured in the soxhlet (30% as compared with values above 50% for the other formulations).

In order to correlate the microstructure of the adhesives with their viscoelastic properties, dynamic viscoelastic measurements were carried out. Fig. 2 shows the variation of storage and loss modulus and the damping factor with the frequency at 23 °C. All formulations presented storage modulus values below 0.1 MPa and a value of $\tan\delta/G' > 5 \text{ MPa}^{-1}$, namely, the values recommended for having a good contact in a short time in stainless steel substrates [20,21].

It can be observed that all formulations presented higher values of both G' and G'' than those ones for formulation A. Nevertheless, this formulation showed the best relationship between elastic and viscous behavior, yielding the best energy dissipation (highest $\tan\delta/G'$ value). The storage modulus was especially high in formulation A.1 because of the high molar mass of the insoluble fraction (see Fig. 1, green line), which affected the motion of the polymer chains and, therefore, the energy dissipation. The solid-like behavior of the adhesive decreased in formulation A.2, providing a lower value for the storage modulus and, consequently, higher $\tan\delta/G'$. Although similar values of storage modulus (G'), in the whole range of frequencies, were obtained for formulations A.2 and A.3, the damping factor ($\tan\delta$) was higher for the

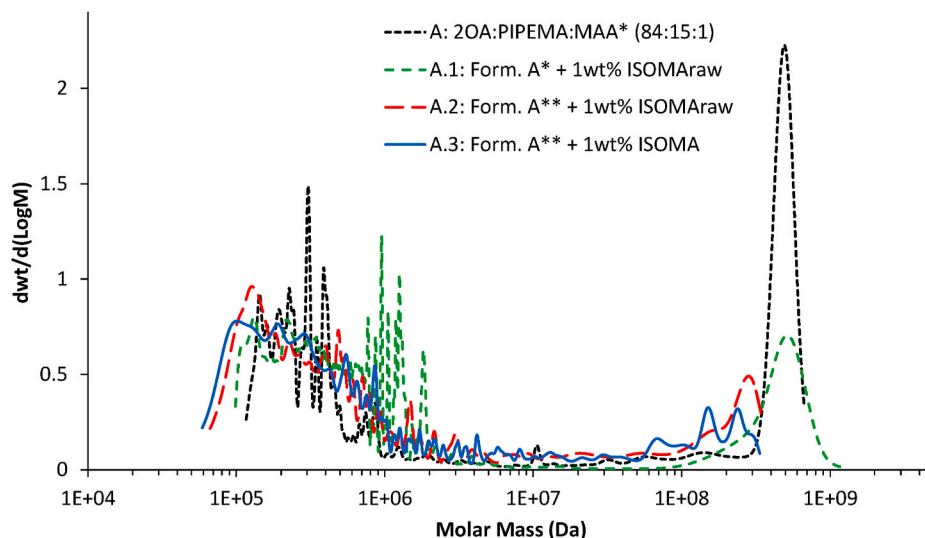


Fig. 1. Molar mass distributions measured by AF4/MALS/RI for the four latexes of this work. See Table 2 for the compositions of each formulation.

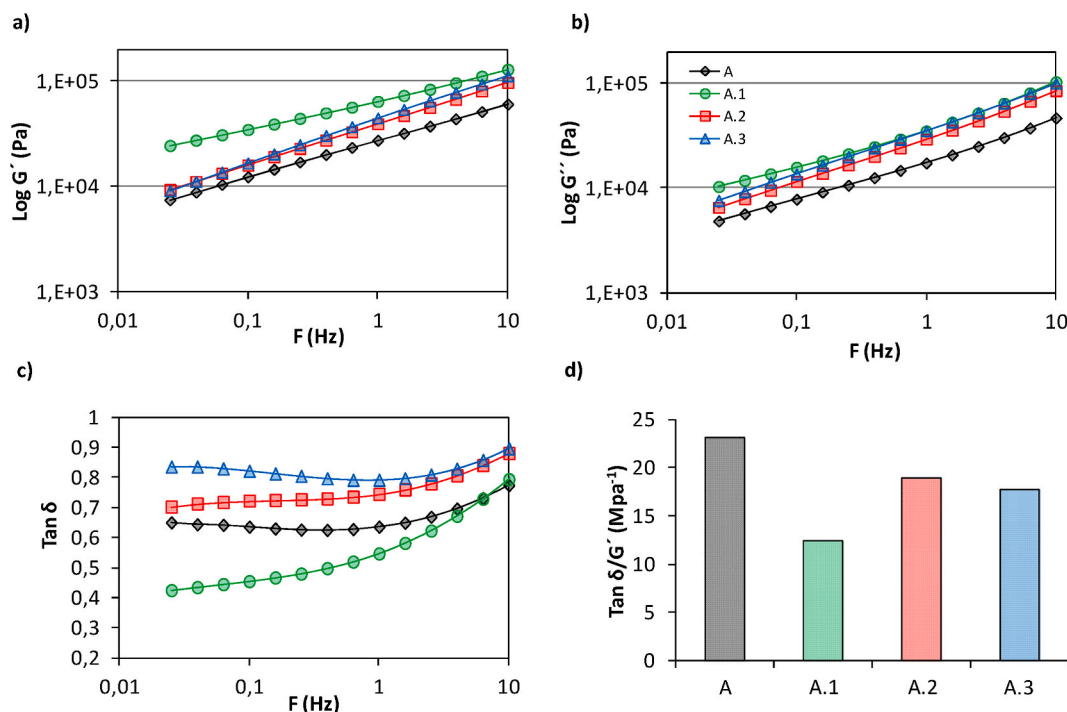


Fig. 2. (a) Storage modulus (G'), (b) loss modulus (G''), (c) dynamic modulus ($\tan\delta$) and (d) $\tan\delta/G'$ for 20A:PIPEMA formulations containing ISOMA or ISOMArAw as functional monomer. Measurements made at 23 °C and 1 Hz.

Table 2

Properties of the PSA latexes containing 20A:PIPEMA as main formulation.

PSA	Composition (%wt monomers)	dp (nm)	Gel (%) [†]	Tg (°C)	Bio (%)
20A:PIPEMA: ISOMArAw:MAA					
A*	84:15:0:1	231 ± 4	53 ± 2	-38	71
A.1*	84:14:1:1	234 ± 3	58 ± 0.1	-36	71
A.2**	84:14:1:1	232 ± 4	50 ± 1	-36	71
20A:PIPEMA: ISOMA:MAA					
A.3**	84:14:1:1	231 ± 2	32 ± 0.5	-36	71

* and ** make reference to 0.025 wbm% and 0.075 wbm% of 2EHTG and 1BuSH, respectively.

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

Table 3

Adhesive properties of the PSA tapes containing 20A:PIPEMA as main formulation.

PSA	Composition	180° Peel (N/25 mm)	Loop tack (N/25 mm)	WA [#] (J/m ²)	Shear resistance (min)	SAFT (°C)
20A:PIPEMA: ISOMArAw:MAA						
A*	84:15:0:1	7.9 ± 0.7	10 ± 0.1	197 ± 32	90 ± 10	64 ± 5
A.1*	84:14:1:1	6 ± 0.8	11.8 ± 1.4	222 ± 23	75 ± 15	88 ± 1
A.2**	84:14:1:1	8.8 ± 0.2	10.9 ± 1.3	202 ± 24	150 ± 30	52 ± 1
20A:PIPEMA: ISOMA:MAA						
A.3**	84:14:1:1	9.6 ± 1	15.4 ± 2	282 ± 29	35 ± 5	48 ± 1

* and ** makes reference to 0.025 wbm% and 0.075 wbm% of 2EHTG and 1BuSH, respectively. # Work of adhesion calculated from the area under the curve of the loop tack test.

latter. This might be related with the presence of several low molar mass polymer chains (Fig. 1, range 4×10^4 - 10^6 Da, blue line) promoting the liquid-like behavior. However, similar values of $\tan\delta/G'$ at the debonding frequency were obtained for these formulations (Fig. 2d) because of the compensation between G'' and G' . It is worth pointing out that formulations containing PIPEMA present a remarkable dissipation of energy at the interface adhesive-substrate (as compared with identical formulations using isobornyl methacrylate, IBOMA, instead of PIPEMA [17]) because of the greater viscous behavior that piperonyl

methacrylate comonomer provides to the polymer networkG.

The adhesive properties of these four latexes are shown in Table 3. The presence of ISOMArAw in formulation A.1 reduced the peel strength but increased loop tack and work of adhesion (WA) because of a higher fraction of lower mass polymer chains of the low molar mass peak (Fig. 1, range 10^5 - 10^6 Da, green line). In formulation A.2, the peel force increased to 8.8 ± 0.2 N/25 mm as consequence of the good balance between the chains motion and the cohesion among them, keeping good values of both loop tack and work of adhesion, but suffering a decrease

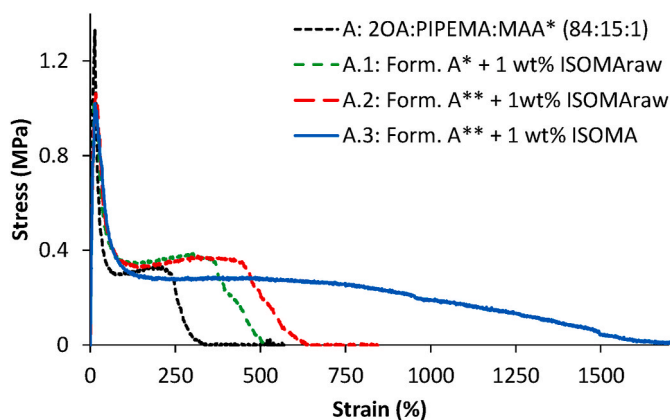


Fig. 3. Probe tack tests for 2OA:PIPEMA formulations.

in the holding temperature. Formulation A.3 (with only ISOMA monomer) led to a remarkable increase of the tackiness as well as the work of adhesion, reaching a value of $282 \pm 29 \text{ J/m}^2$ without leaving the rest of the adhesive on the substrate surface. Peel strength also increased, getting a force value close to 10 N/25 mm , which means that cohesiveness among the polymer entanglements is still enough during the debonding process, getting a similar holding temperature but affecting shear resistance [22].

Fig. 3 shows the probe tack curves for these formulations (the steps of a typical probe tack curve are explained in the Supporting Information). As can be appreciated the incorporation of ISOMArAw provided adhesive fibers with higher elongation at break capable of holding greater stress in comparison with formulation A. Regarding this, the combination of a covalent crosslinked polymer network (the high molar mass mode) together with the presence of low molar mass polymer chains enhanced not only the cohesiveness of the fibrils but also their extensibility [23]. The reduction of the solid-like behavior in formulation A.2 resulted in a slight decrease of the plateau height followed by a longer elongation at break as a consequence of the better dissipation of energy. Note that the good relationship between G' and G'' promoted the extensibility of the adhesive fibrils without affecting their cohesion in a relevant way. Lastly, the use of ISOMA in formulation A.3 led to a remarkable increase of the viscous component and, hence, a great enhancement of the extensibility of the adhesive fibrils which broke at 1500% of strain and not leaving any adhesive residue on the probe. The decrease in the molar mass of the high molar mass peak as well as its amount (lower gel content) favor the reduction of the polymeric network cohesiveness. This led to a progressive diminution of the stress supported by the fibers along the strain. It is worth mentioning that all

formulations presented adhesive failure, which is the desired mode of failure during the debonding process.

Aiming to assess if small fractions of this isosorbide derivative monomer (ISOMArAw or ISOMA) promoted the water sensitivity of the present adhesive tapes, removability studies were performed by measuring the peel strength of the adhesive films adhered on glass after immersion in deionized water over time (at room temperature and at 65°C). Notably, the hydrophilicity of isosorbide functional monomers (ISOMArAw or ISOMA) allow their incorporation on the surface of the polymer particles. Thus, during film formation, part of the OH groups of the particle will be located at the air-adhesive film interface. These free hydroxyl groups may interact with silanol groups (on 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). A scheme of this process is illustrated in the supporting information (Scheme S1). Fig. 4 shows the peel force values of the films immersed in deionized water for different times. The faster the decay of the peel force with immersion time the easiest is the removability of the adhesive tape; namely, the higher the removability rate (the slope of the peel force versus time curves). As for 2OA/IBOMA/ISOMArAw PSAs [17], 1 wt% of ISOMArAw/ISOMA allowed the complete detachment of the adhesive tape from the glass in less than 40 min at room temperature and around 10 min at 65°C (Fig. 4b). Furthermore, formulations A.2 and A.3 showed the highest values of peel strength with a similar removability rate in water without leaving residues on the substrate surface.

3.1. Effect of the UV-light irradiation time on the adhesive properties

Notably, the incorporation of small amounts (1 wt%) of these isosorbide methacrylate monomers yielded bio-based PSA tapes with improved adhesive performance as well as an enhancement of the removability from glass substrates at mild conditions. This enhancement of the properties was also observed for bio-based waterborne adhesives containing IBOMA instead of PIPEMA as hard monomer [17]. However, the bio-based PSA tapes containing IBOMA presented better cohesiveness; thus substantially higher shear resistance (up to 1500 min) and higher holding temperatures (up to 157°C) for similar formulations.

Interestingly, piperonyl methacrylate presents a benzodioxole moiety and, as demonstrated recently, crosslinking reactions may be promoted upon UV-light treatment via radical rearrangement [24–26]. Specifically, the active hydrogen between the two alkoxy groups of dioxole moieties can be abstracted as a radical under photolytic conditions. Those cyclic acetal radicals generated are rearranged rapidly by β -scission forming the corresponding ester and, thereafter, a termination by combination of the formed radicals affords the crosslinked structure. Scheme 2 shows the photoreaction mechanism for adhesive films

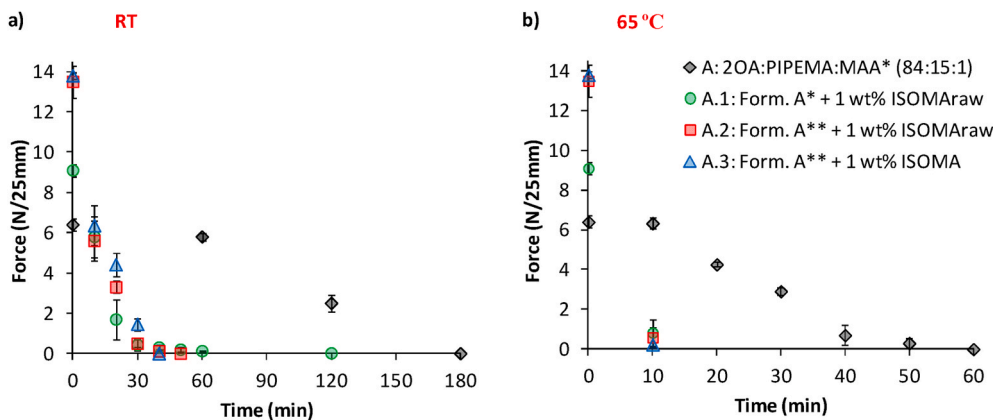
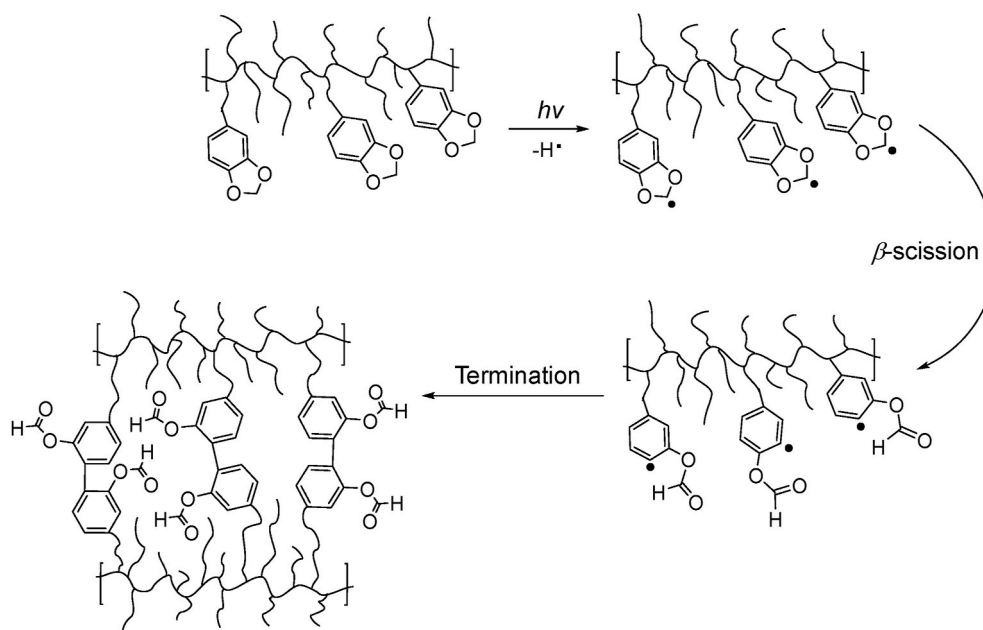


Fig. 4. Evaluation of 180° peel strength at different times of water treatment at room temperature (a) and at 65°C (b) on glass for PSA tapes containing 2OA:PIPEMA as main formulation and ISOMA or ISOMArAw as functional monomer.



Scheme 2. Photoreaction mechanism for adhesive films containing PIPEMA (reprinted with permission from ACS from reference 16).

containing PIPEMA.

We have reported that waterborne bio-based PSA tapes containing PIPEMA substantially improved shear resistance and holding temperature, when the adhesive film was irradiated with UV light between 15 and 30 min [16]. Thus, increasing irradiation time, the crosslinking density of the adhesive film increased. This was assessed by measuring the swelling degree (inverse of the crosslinking density) and the relaxation time of the films by ^1H NMR in reference 16. Herein and as representative example of this mechanism, the swelling degree as a function of the irradiation time for formulation A is included in the supporting information (see figure S2 that shows how the swelling degree of the films decrease with irradiation time). With this result in mind, we analyzed in formulation A.3, which presented excellent peel resistance and work of adhesion, though poor shear resistance, if cohesiveness could be improved by post-irradiating the adhesive film with UV light. Furthermore, we analyzed if the facile removability of the adhesive in water in mild conditions was preserved after the UV treatment. This is of particular interest in order to provide an easily removable, high bio-content adhesive tape whose cohesive performance can be adjusted as a function of the curing time.

The adhesion properties of films of latex A.3 irradiated at 254 nm for 15, 30, 60 and 120 min were measured. Note that above 60 min of irradiation, PSA tapes became yellowish because of the formation of conjugated phenolic structures [27]. Table 4 summarizes the adhesion properties of those films at different irradiation times. As the irradiation time increased, peel strength, loop tack and work of adhesion decreased due to the generation of a more crosslinked polymer that likely increased storage modulus (see Figure S2 in the supporting information that shows the increase of the storage modulus of films of formulation A with irradiation time) and thus reduced adhesiveness. On the contrary, shear resistance and holding temperature experienced an increase due to the

enhancement of the solid-like behaviour (higher storage modulus) of the PSA. It is worth pointing out that 15 min of UV-light irradiation increased around 100 times the shear resistance and 40 °C the holding temperature only weakly affecting the adhesion of the tape (peel resistance slightly reduced but work of adhesion was reduced to half).

Fig. 5 shows the evolution of the probe tack curves upon the UV-light irradiation time. It can be noted that 15 min of irradiation provided less extensible but more rigid adhesive fibrils, yielding a higher fibrillation plateau with an elongation at break close to 1000% of strain. This behavior corresponds to a slight increase in the solid-like behavior (as discussed above due to the higher crosslinking density) that enhances the cohesiveness of the fibrils, but ensuring a good enough extensibility among them. However, as the irradiation time increased the length of the fibrillation plateau decreased substantially, showing similar shapes for the probe tack curves above 30 min with elongations at break close to 600% of strain. This is in agreement with the observed reduction of tackiness and peel strength because of the increase in the crosslinking density, which promoted both the holding temperature and shear resistance. This promotion of the solid-like behavior with the irradiation time offers an adhesive material suitable for a wide range of industrial applications.

Removability studies at mild conditions were carried out in order to verify if the water affinity of the isosorbide derivative monomer was preserved despite the increase in the crosslinking degree. Fig. 6 shows the evolution of the peel strength after water immersion at 25 °C for the PSA tape irradiated for 15 min. It was confirmed that the removability (totally removed in 30 min) of the adhesive on the glass substrate was preserved after the irradiation with UV for 15 min. Note that UV-light irradiation mainly affects the bulk structure of the polymer film promoting crosslinking reactions between benzodioxole moieties. Therefore, this does not have a relevant impact on the surface of the adhesive

Table 4

Adhesive properties of the PSA tapes containing the formulation 20A:PIPEMA:ISOMA:MAA** (84:14:1:1) cured at different irradiation times at 254 nm.

UV Irradiation time (min)	180° Peel (N/25 mm)	Loop tack (N/25 mm)	WA (J/m ²)	Shear resistance (min)	SAFT (°C)
0	9.6 ± 1	15.4 ± 2	282 ± 29	35 ± 5	48 ± 1
15	8.7 ± 1.1	8.6 ± 1.2	132 ± 6	3200 ± 100	80 ± 15
30	6.9 ± 0.4	7.3 ± 0.1	125 ± 6	7500 ± 300	126 ± 4
60	3 ± 0.6	4.1 ± 0.3	71 ± 4	>10080	138 ± 5
120	1.8 ± 0.9	1.6 ± 0.3	15 ± 2	>10080	142 ± 5

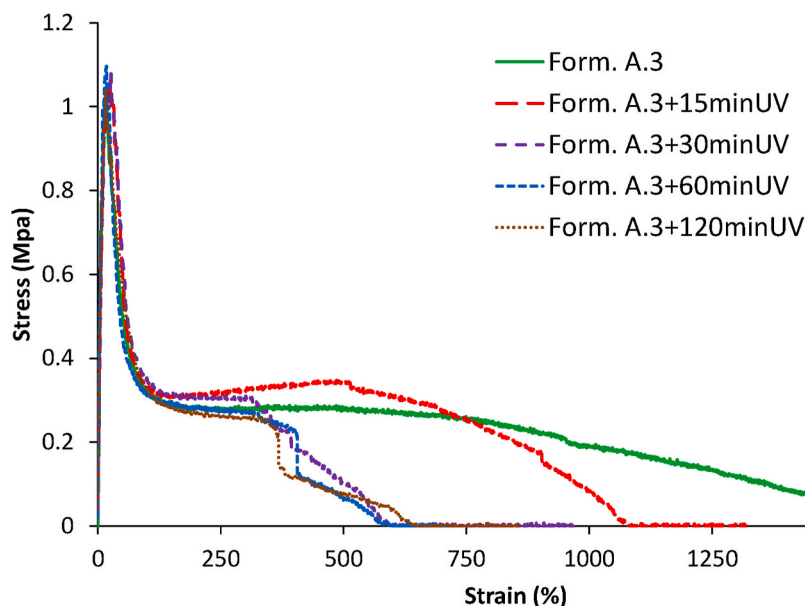


Fig. 5. Probe tack tests for formulation A.3 cured at different irradiation times using 254 nm of wavelength.

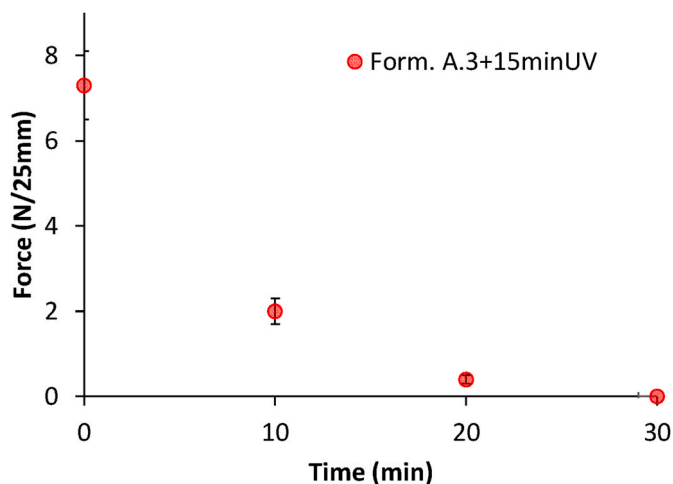


Fig. 6. Evaluation of 180° peel strength after different times of immersion in deionized water at room temperature on glass for PSA tape irradiated at 15 min.

film, where free hydroxyl groups are located, keeping the removability efficiency in water non-affected (see comparison between Fig. 4 (a) and Fig. 6 for formulation A.3 before and after irradiation, respectively).

4. Conclusions

In this work, we have explored the combination of two novel functional biobased monomers in the synthesis of high bio-content (71%) waterborne pressure sensitive adhesives. It was found that small amounts (1 wt%) of isosorbide methacrylate monomer (either ISOMArAw or ISOMA) enhanced both the extensibility and cohesiveness of the adhesives fibrils in PSA formulations containing PIPEMA as hard monomer and 2OA as soft counterpart. This sugar-based derivative monomer not only increased the performance of the adhesive tape, but also its fast removability in water. The tapes completely detached from the glass substrate after 40 min of immersion at room temperature and in 10 min at 65 °C. Furthermore, the presence of piperonyl moieties in the PSA formulation allowed the fine-tuning of the crosslinking degree of the adhesive film upon UV-light irradiation time. Thus, 15 min of irradiation promoted the cohesiveness of the fibrils with moderate impact

on the adhesion properties, namely, on tackiness and peel strength. Furthermore, the increase of the crosslinking density of the films after UV irradiation did not affect water sensitivity of the PSA tape. Notably, biobased adhesives with a tunable adhesive performance and easy removability from glass substrates are synthesized by combination of novel biobased monomers ISOMArAw and PIPEMA as functional monomer and hard monomer, respectively.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijadhadh.2021.102860>.

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