Incorporation of novel degradable Oligoester Crosslinkers into Waterborne Pressure Sensitive Adhesives: Towards removable Adhesives

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Abstract

Waterborne pressure-sensitive adhesives containing degradable crosslinked chains that enable easy removability of the adhesive tape have been successfully synthesized. Symmetric and asymmetric degradable oligoester crosslinkers of variable chain length have been synthesized by ring opening polymerization (ROP) of ε-caprolactone and lactide. The oligoester crosslinkers have been incorporated into a conventional waterborne PSA formulation to demonstrate the possibility of introducing degradability by hydrolysis of crosslinking chains to PSAs. The adhesive films present good adhesive properties, but it is remarkable that when exposed to basic conditions their adhesion is substantially reduced within short times and hence the PSAs can easily be removed (much easier than if conventional crosslinkers are used). The degradation of the ester group of the crosslinkers is responsible for the loss of adhesion properties making this kind of degradable waterborne PSAs excellent candidates as removable adhesives. These PSAs might have a strong impact on the sustainability of the cleaning process of glass bottles (or other substrates) by reducing the energy and solvent consumption.

Introduction

One of the most important challenges of the 21st century is to diminish the amount of residues produced by humans. The World Bank predicts that the yearly-generated amount

of municipal solid waste is going to increase from 1.3 billion tons up to 2.2 billion tons in the year 2025. Next to organic, paper and plastic waste, glass waste makes up for 5% of the global solid waste composition.[1] Glass bottles and jars are 100% and infinitely recyclable.[2] However, for example in the US in the year 2015 only 33.2% of the waste glass were recycled.[3] Even better than recycling, which means crushing the glass into glass cullet and manufacturing new glass from the glass cullet, would be reusing glass bottles. According to the annual worldwide production, around 5 billion of glass bottles could be reusable. Returned bottles are cleaned in bottle cleaning machines at temperatures of around 85 ºC using additives containing a basic solution (e.g., sodium hydroxide). During the cleaning process the labels and adhesives of the glass bottles have to be removed[4] and for that the exposure to heat, jetted hot gas or sprayed hot liquid having a predetermined temperature is necessary.[5] Another method for removing bottle labels and adhesives is the usage of amidine solvents such as 1,8-diazobicyclo[5.4.0]undec-7-ene (or DBU) or fatty N,N-dialkylamides as described elsewhere.[6] All in all, the described industrial processes are either energy intensive or require the use of toxic chemicals. An adhesive providing the required performance that would easily degrade during the bottle cleaning process within milder conditions might be able to overcome this issue.

Hence, a balance between stability during the shelf-life of the adhesives and their (bio)degradability after their disposal is of great importance. Main degradation processes consist of biodegradation, atmospheric oxidation and hydrolysis.[7,8] Thus polyesters possess a big potential because of their structural diversity, the possibility to be degraded by water-degradation (hydrolysis) or biodegradation and furthermore, many of them are accessible from natural building blocks.[9] Ester groups can be incorporated into polymers in several ways: As grafted sidechains,[10,11] directly into the polymeric backbone for example by (radical) ROP[12,13] and by thiol-ene polymerization,[14,15] or as oligoester chains crosslinking unsaturated carbon chains as reported in this work.

PSAs are viscoelastic materials that can adhere strongly to solid surfaces upon application of a light contact pressure and in short contact times.[16] They can achieve instantaneous adhesion to a surface without activation and by having sufficient internal strength not to break up before the bound between the adhesive and the surface ruptures.[17] In a typical waterborne PSA formulation, apart from the monomers, emulsifier, initiator and water, crosslinkers and chain transfer agents (CTA) can be used to balance the cohesive and

adhesive forces of the film, respectively.[18] The PSA sector is among the fastest growing ones in the adhesive market.[19] Within the different base polymers for making PSAs, waterborne acrylates are the fastest growing ones for commercial applications.[16] Therefore, new formulations with improved adhesivity, degradability or stimuli-responsive characteristics are of great interest.[20]

Different approaches to obtain degradable polymer nanoparticles have been published in the literature. Sato et al. demonstrated the first strategy to obtain degradable PSAs. They synthesized two types of degradable polyperoxide PSAs. On the one hand through the synthesis of linear polyperoxides from methyl sorbate and oxygen, and on the other hand through the oxygen crosslinking of dienyl functionalized poly(ethylene glycol) to obtain peroxide groups within the crosslinks. Degradation was proved at raised temperatures and under UV-light.[21] However, due to the solvent used during the synthesis as well as the energetic conditions needed, it can be concluded that these materials do not meet the criteria of the previously mentioned environmentally friendly products.

Another approach reported by Ferrari et al. is based on the synthesis of degradable oligoester macromonomers. The macromonomers were prepared by ROP using 2-hydroxyethylmethacrylate as initiating species and lactide[22] and ε-caprolactone as monomers. The degradability over time of waterborne particles obtained through emulsion homopolymerization of the macromonomers was proven by measurements of pH and particle size indicating a complete degradation of the particles within 6-9 months.[23] However, the solids content of the waterborne dispersions were low (5 wt%) and moreover, they were only applied for drug delivery[24–28]. Later, Pu et al. demonstrated the usage of the same kind of macromonomers and co-macromonomers of lactide and ε-caprolactone in copolymerizations with commercial acrylates, such as *n*-butylacrylate (BA) by miniemulsion polymerization for the synthesis of PSAs.[29] Even, if they demonstrated that the PSA containing macromonomers performed as the commercial ones in terms of peel and shear properties, the loop tack was worse. Nonetheless, they did not show any degradability test of the adhesives.

Very recently, a different approach was introduced by Beharaj et al. to synthesize PSAs. They inserted CO_2 into a polyacrylic backbone forming poly(carbonate) analogues which were degraded depending on time and pH, but in all cases during large periods of time (between 4-32 days).[20] Moreover, as the molecular weights of the PSA were quite low, the final adhesive performance was not as good as the commercial ones.

On the other hand, recent patent literature describes the synthesis of (bio)degradable oligoester crosslinkers for the synthesis of degradable hydrogels.[30,31] Besides, another patent describes the synthesis of degradable PSAs by copolymerization of (meth)acrylic monomers and alkyl acryloxy glycolate monomers[32]. In this work they describe the possibility to use the degradable oligoester crosslinkers of references [30] and [31] for the synthesis of degradable PSAs. Nevertheless, these oligoester crosslinkers are produced by a multiple step synthesis, which requires purification steps of the products making it time and energy consuming.

It should be mentioned that these types of oligoester macromonomers and crosslinkers have been used in other types of applications such as in the production of graft coatings or degradable hydrogels for biomedical applications.[11,33]

Herein, we present a family of novel degradable crosslinkers that can be used to produce removable waterborne PSAs, which excels by, despite its simplicity to be integrated into already existing processes, bearing the potential to have a positive effect on the greenness and sustainability of the recycling processes of substrates with attached PSAs and labels (e. g. glass bottles). Thus, oligoester crosslinkers were synthesized in a one pot synthesis by ROP reaction using 2-hydroxyethylmethacrylate or 1,4-butanediol as initiating species and lactide, ε-caprolactone and itaconic anhydride as monomers, which does not require any kind of purification of the products. Oligoester crosslinkers with a target number of lactide and ε-caprolactone units were synthesized with symmetric and asymmetric vinyl functionality. These crosslinkers were incorporated into a waterborne PSA formulation using a seeded semibatch emulsion polymerization process obtaining high solids content latices (of 50 wt% solids content). The synthesized waterborne PSAs using the degradable crosslinkers showed good adhesive performance (measured as probe-tack, shear resistance and peel resistance). The influence of the number of lactide and ε-caprolactone units to the adhesive performance, degradability and removability was also investigated.

Experimental section

Materials

2-Hydroxyethyl methacrylate, HEMA, (Sigma Aldrich), 1,4-butanediol (Sigma Aldrich), lactide (Alfa Aeser), ε-caprolactone (Sigma Aldrich), itaconic anhydride (Alfa Aeser) and tin(II) 2-ethylhexanoate (SnOct$_2$, Sigma Aldrich) were used as received for the synthesis of the macromonomers. n-butyl acrylate, BA, (Quimidroga), methyl methacrylate, MMA, (Quimidroga), sodium bicarbonate (Sigma Aldrich), acrylic acid, AA, (Sigma Aldrich), potassium persulfate, KPS, (Sigma Aldrich), *tert*-dodecanethiol, t-DDM, (Fluka), dodecyl diphenyloxide disulfonate (Dowfax 2A1 45%, Dow Chemicals) and ammonium hydroxide solution (28% NH$_3$ in H$_2$O, Sigma Aldrich) were used in emulsion polymerization without further purification. Deionized water was used in the emulsions and hydroquinone (Acros) was used for stopping the polymerization of the withdrawn samples. HPLC grade tetrahydrofuran (THF, Scharlab) and technical grade THF (Scharlab) were used as received for Gel Permeation Chromatography (GPC), Asymmetric-Flow Field-Flow Fractionation (AF4) and soxhlet extraction, respectively. Potassium hydroxide solution (1 mol%, Sigma Aldrich) was used as a base for the degradation studies.

Synthesis of Crosslinkers

Asymmetric and symmetric oligoester crosslinkers with different target chain-lengths were synthesized by ROP using SnOct$_2$ (0.1 mol%) as a catalyst in bulk under nitrogen atmosphere. The synthesis of the crosslinkers was started either with HEMA (asymmetric crosslinkers) or with 1,4-butanediol (symmetric crosslinkers) as initiating species. The monomers ε-caprolactone and lactide were used in different ratios at a temperature of 130 ºC for 6 h. In a second step, 1.1 or 2.2 equivalents (regarding the oligoester chains) of itaconic anhydride were added, for asymmetric and symmetric crosslinkers respectively, and the temperature was kept at 90 ºC for 3 h. See Scheme 1 and 2 for more details.
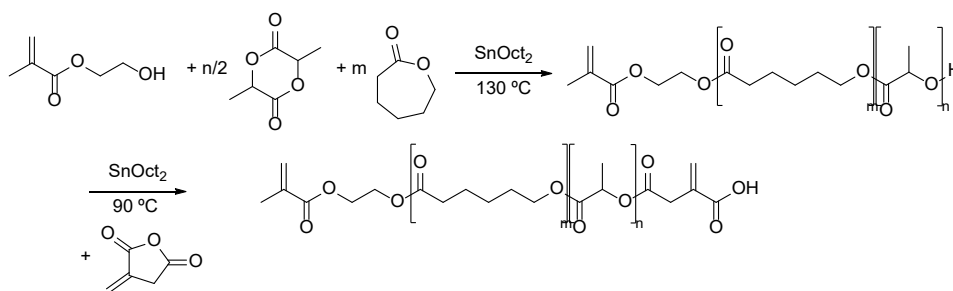
Scheme 1: ROP synthesis of asymmetric crosslinkers.
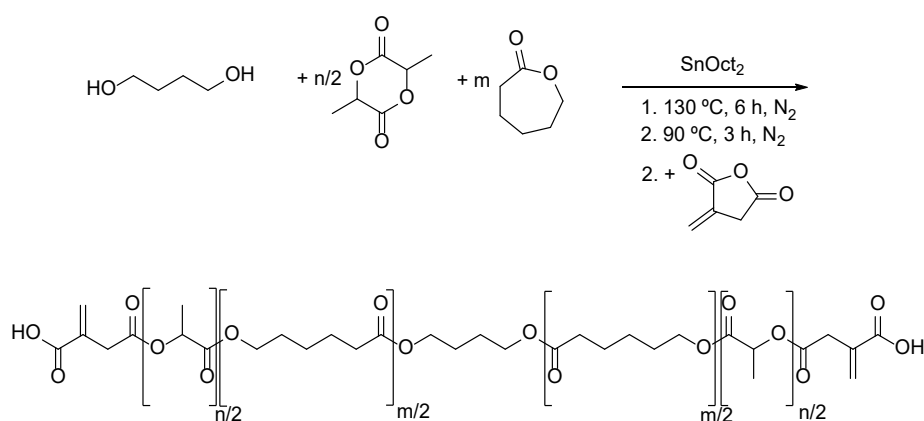
Scheme 2: ROP synthesis of symmetric crosslinkers.

The asymmetric and symmetric oligoester crosslinkers are referred to as ASY-LAnCLm and SY-LAnCLm in which n and m indicate the number of lactic acid and ε-caprolactone units, respectively.

PSA Synthesis by Seeded Semibatch Emulsion Polymerization

PSAs were synthesized in a two step seeded semibatch emulsion polymerization process (see Supporting Information for the formulations of the seed and the seeded semibatch process). First, a seed with a solids content of 30% was prepared by semibatch emulsion polymerization. Surfactant (Dowfax 2A1), water and ammonium hydroxide solution were loaded into a 1 L glass reactor and heated to the reaction temperature (80 ºC). Subsequently, the initiator (KPS) was added and a preemulsion containing the monomers BA, MMA and AA (in the ratio 89.1/9.9/1), surfactant (Dowfax 2A1) and water was fed with a flow rate of 1.59 g/min for 180 min to the reactor. After finishing the feed, the reactor was maintained at 80 ºC for additional 60 minutes.

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In a second step, acrylic latices with a solid content of 50 wt% were prepared by seeded semibatch emulsion polymerization at a temperature of 75 ºC and under nitrogen atmosphere. The seed and water were loaded into a 1 L glass reactor. The initiator (KPS) and the buffer (sodium bicarbonate) were added as a shot as soon as a temperature of 75 ºC was reached. Then the preemulsion containing the monomers BA, MMA, AA (in the ratio 89.1/9.9/1), oligoester crosslinkers (0.2 mol%), t-DDM, surfactant (Dowfax 2A1) and water were fed at a flow rate of 1.35 g/min in 180 min. The temperature was raised and kept at 80 ºC for 60 min after the feeding was finished.

Characterization

Polymer particle sizes were analyzed by dynamic light scattering (DLS) using a Zetasizer Nano Series (Malvern Instruments). Conversion was determined gravimetrically. The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC, Q1000, TA Instruments) of dry polymers from the final latexes using hermetic pans. The gel fraction (or insoluble fraction of the copolymer in THF) was measured by Soxhlet extraction and the molar mass distribution of the soluble fraction was determined by GPC. The GPC set up consists of a pump (LC-20A, Shimadzu), an autosampler (Waters 717), a differential refractometer (Waters 2410) and three columns in series (Styragel HR2, HR4 and HR6) with pore sizes ranging from 10^2 to 10^6 Å. Measurements were carried out at 35°C and referred to polystyrene standards. Moreover, the entire molar mass distributions of the latices were determined by asymmetric-flow field-flow fractionation (AF4, Wyatt Eclipse 3) using a multi-angle light scattering (MALS) and a refractive index (RI) detector and THF as solvent. A pump (LC-20, Shimadzu) coupled to a DAWN Helios multiangle light scattering laser photometer (MALS, Wyatt) equipped with a HE-Ne laser (λ = 658 nm) and an Optilab Rex differential refractometer (λ = 658 nm) (RI, Wyatt Technology). ASTRA 6 software (Wyatt Technology) was used for the data collection and treatment. 10 mg of the latices were dispersed in 1 mL of THF for the preparation of the samples. 50 µL of this solution were injected for the measurement. The Debye plot with second-order Berry formalism was used to calculate the molar mass from the RI/MALS data.

Film preparation

Adhesive films were prepared by casting the latex on a flame treated polyethylene terephthalate (PET) sheet (29 μm thick) using a stainless steel film applicator. The film applicator was used with a gap of 120 μm to produce films with a thickness of approximately 60 μm. For the probe tack measurements, films with a final thickness of 100 μm were casted over a glass substrate. In all the cases, films were dried at 23 ºC and 50% humidity for 12 h.

Adhesive properties

The adhesive properties of the latices were characterized using different methods. The peel resistance, loop tack and probe tack tests were performed with a TA.HD Plus Texture Analyzer (Texture Technologies, Hamilton, MA, USA) at 23±2 ºC and 50±5% humidity. The shear resistance failure time and the holding temperature were tested using Shear/SAFT equipment (Sneep Industries). Shear measurements were carried out at a temperature of 25 °C. A temperature ramp of 1 ºC/min was applied for the SAFT measurements and a weight of 1 kg was attached to the samples for shear and SAFT measurements. For all the cases, average values of four repeated measurements are reported in this work. As for the rheological behaviour of the latices, dynamic mechanical analysis (DMA) was performed with an Anton Paar rheometer using parallel plate geometry. Frequency sweeps (0.3-120 rad s^{-1}) with an applied strain between 0.5% and 2% were made on 500 μm thick samples of 8 mm as diameter at 23 ºC. An extended description for the characterization of the adhesive properties is provided in the Supporting Information.

Degradation studies

100 μm films were prepared on glass substrates and immersed into a potassium hydroxide solution with a pH of 10. Every 15 min they were taken out of the potassium hydroxide solution, dried for approximately 1 h and probe tack measurements were performed. The work of adhesion was calculated by integration of the probe tack curves. The average value of 4 measurements for each immersion time is reported.

30 μm films were prepared on a paper label substrate. The paper label with the film was then attached to a glass bottle. The glass bottle with the attached label and PSA film was immersed for 24 h into a potassium hydroxide solution at a pH of approximately 10. As a reference sample, the same procedure was carried out with a commercial wine bottle with its label and commercial PSA. After the immersion time, the removal of the labels was tried, by peeling of the labels by hand.

Results and Discussion

Asymmetric and symmetric crosslinkers were successfully synthesized by a one-pot ring opening polymerization process. Three different asymmetric crosslinkers and two symmetric ones were synthesized changing the ratio between lactide and ε-caprolactone and hence, changing the length. For all the cases, the theoretical molar mass and the experimental ones measured by either NMR or GPC were very similar confirming the desired structure of the crosslinkers (see Table 1 and Supporting Information for the NMR spectra). The number average molar masses measured by GPC show a slight deviation from the theoretical ones, which could be attributed to the polystyrene calibration used in the analyses of the data.

Table 1: Summary of the synthesized asymmetric and symmetric crosslinkers and their theoretical and experimental molar masses calculated from NMR and number-average molar mass (Mn) determined by GPC.

Crosslinker	M (theo.) [g/mol]	M (NMR) [g/mol]	M_n (GPC) [g/mol]	PDI
ASY-LA2CL2	598	586	503	2.0
ASY-LA4CL4	986	1118	1078	1.9
ASY-LA8CL4	1274	1274	1464	1.7
SY-LA2CL2	686	680	574	1.6
SY-LA6CL6	1486	1486	1583	1.4

The next step was the incorporation of the degradable crosslinkers into waterborne PSA formulations (MMA/BA/AA in the weight ratio 89.1/9.9/1) by a two step seeded semibatch emulsion polymerization process. An amount of 0.2 mol% of the crosslinkers was used in the second step of the seeded semibatch emulsion polymerization. For the sake of comparison, two more latices were synthesized, one without crosslinker and the

other one using the conventional commercially available crosslinker allyl methacrylate (AMA). The evolution of the instantaneous and overall conversions and the intensity-average particle sizes along the reaction are shown in Figure 1 a) and b).
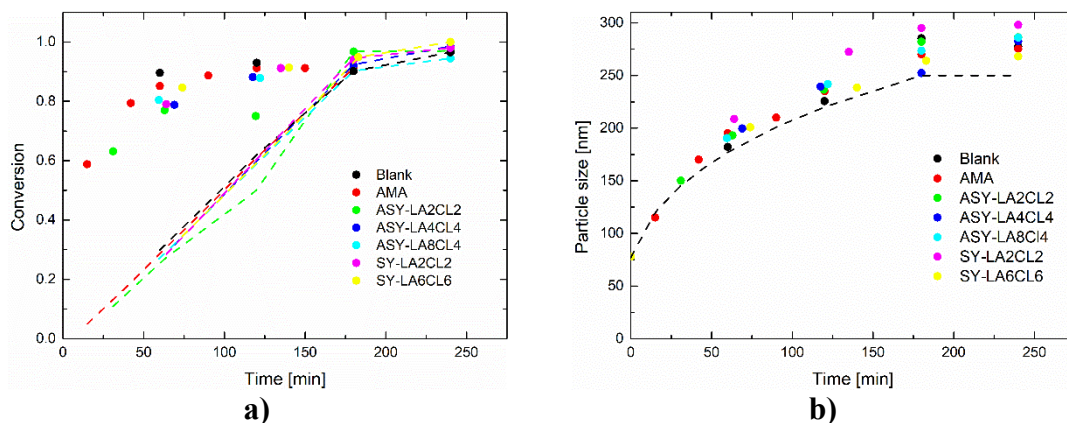

a)   b)

Figure 1: a) Instantaneous (dots) and overall monomer conversions (dashed lines) of the seeded semibatch experiments containing different crosslinkers. b) Evolution of the intensity-average particle size (dots) measured by DLS and the theoretical evolution of particle size (dashed line) for the same experiments.

The kinetics were very similar in all the cases regardless of the type of crosslinker used. Instantaneous conversions were above 80% during most of the time and at the end almost full conversion was achieved in all the cases (see Table 2). Regarding the average particle size evolution, it can be seen that there were not substantial differences either, having final particle sizes between 270-300 nm. In all the cases, the average particle size was larger than the target one indicating some aggregation or coagulation between particles towards the end of the polymerization process.

One of the most important properties of a PSA is their T_g. As it can be seen in Table 2, all the synthesized latices presented similar and appropriate T_gs to use them as PSA, between -36 ºC and -33 ºC.

Table 2: Conversion, intensity-average particle size (D_p), glass transition temperature (T_g), gel content measured by Soxhlet ($GC\ S$), weight-average molar mass (M_w) of the soluble part in THF and dispersity index results for PSA latices with different crosslinkers.

Crosslinker	χ [%]	D_p [nm]	T_g [ºC]	$GC\ S$ [%]	$Sol\ M_w$ [g/mol]	Đ
Blank	96	278	-36	7 ± 7	178100	2.1
AMA	98	276	-34	74 ± 0.3	78800	2.2
ASY-LA2CL2	97	295	-34	40 ± 1	232600	3.4
ASY-LA4CL4	99	283	-33	34 ± 0.5	238220	4.3

ASY-LA8CL4	99	286	-34	31 ± 0.2	271800	4.5
SY-LA2CL2	100	298	-34	40 ± 0.3	263600	4.1
SY-LA6CL6	100	268	-34	23 ± 0.6	270400	3.6

As for the gel content or insoluble part in THF, the blank latex showed almost no gel due to the usage of dodecanethiol as a CTA. This result was expected as it has been reported previously for the emulsion polymerization of acrylates.[34] On the other hand, the latex synthesized using AMA showed the highest gel content of 74%. The gel contents of the latices with the oligoester crosslinkers are between the blank and the one containing AMA. For the asymmetric oligoester crosslinkers the shortest one ASY-LA2CL2 showed the largest gel content of 40% and increasing the length of the asymmetric oligoester crosslinker the gel content decreased. Moreover, a similar trend was found for the symmetric oligoester crosslinkers, where the longest crosslinker led to the lowest gel value of 23%. Even though the same amount of moles (0.2 mol% based on the monomers) of the oligoester crosslinkers and AMA were used, the gel content of the latices synthesized using the oligoester crosslinkers was just about half of the gel content of the AMA sample. Furthermore, the gel content decreases when increasing the length of the oligoester crosslinker. This might be due to the lower water solubility of the oligoester crosslinkers and therefore, the limited ability they may have to diffuse in the aqueous phase. The fact that the gel content decreases with an increase in the oligoester crosslinker length reaffirms this hypothesis.

Regarding the soluble M_w measured by GPC, as expected the lowest value was measured for the latex synthesized with AMA, since it had the highest amount of insoluble fraction. However, not only the M_w of the soluble part of the latices containing the oligoester crosslinkers were higher than the two references (the one without crosslinker and the one with AMA), but also the dispersity values were doubled.

In order to shed more light onto the microstructure of the different latices, the whole molar mass distribution was measured using AF4 technique (Figure 2). Broad and bimodal molar mass distributions were measured in all the cases spanning from 10^4 g/mol up to $3 \cdot 10^8$ g/mol or even $4 \cdot 10^9$ g/mol in the case of AMA. Due to the limitations of the technique, the chains with molar masses below $3 \cdot 10^4$ g/mol were not detected.
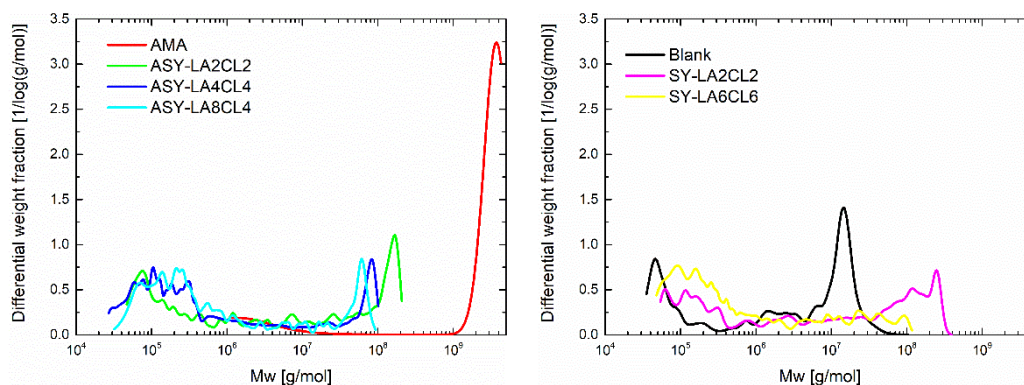
Figure 2: Molar mass distributions of the different PSA latices measured by AF4.

The molar mass distribution of the latex containing AMA (red) presents most of the polymer centered in a narrow peak at extremely high molar mass of $4 \cdot 10^9$ g/mol whereas the blank latex (black) shows a bimodal distribution with a peak at low molar masses $5 \cdot 10^5$ g/mol and a peak at 10^7 g/mol. The latices containing oligoester crosslinkers also present two different populations, one centered at around 10^5 g/mol (in the range of 10^4 g/mol to 10^6 g/mol that likely represents the soluble fraction) and the other one at higher molar masses above 10^7 g/mol (which can be considered as the insoluble fraction in THF). The average molar mass of the high molar mass population shifts to lower values, the longer the oligoester crosslinker is, in accordance with the lower efficiency of the longest oligoester crosslinkers as discussed above. From these molar mass distributions, the gel content can also be estimated assuming a limiting solubility. Thus, considering molecules with molar masses above 10^7 g/mol (note that the GPC analysis of the soxhlet extracted samples does not show molar masses higher than 10^7 g/mol) as gel, the gel contents were calculated from AF4 traces and are reported in Table 3 together with the weight-average molar mass values of the entire sample.

Table 3: Weight-average molar mass of the whole samples and gel content of the latices containing different crosslinkers determined from the AF4/MALS/RI analysis.

Crosslinker	M_w [kDa]	*GC AF4* [%]
Blank	10500	40
AMA	3681000	87
ASY-LA2CL2	76400	43
ASY-LA4CL4	35000	24
ASY-LA8CL4	40079	23
SY-LA2CL2	93800	48
SY-LA6CL6	30900	19

The weight-average molar masses of the entire sample indicate that the lowest molar mass was measured for the blank latex and the highest one for the AMA latex. The weight-average molar masses of the latices containing oligoester crosslinkers showed that the shorter the oligoester crosslinker chain the more efficient was the crosslinker and hence the higher were the weight-average molar masses.

The gel contents determined from AF4 results, except for the blank sample, agree reasonable well with the values and trends measured by soxhlet extraction. The blank sample showed a higher gel content, compared to the result from soxhlet extraction, of 40%. This is likely due to the fact that the high molar mass peak of the blank sample is close to the solubility criteria used to consider what is gel or not from the AF4 measurements, and this criteria might not be accurate for loosely crosslinked gels like for the blank latex. A high gel content of 87% was calculated for the AMA latex on the other hand. The gel contents determined for the latices including oligoester crosslinkers are below the value for the AMA sample and show the same trend as the one measured by soxhlet extraction.

The application of the latices synthesized in this work was to use them as removable PSAs, so they have to flow up to some point in order to make good contact with the substrates. In order to quantify this, the Dahlquist criterion is used which states that PSAs need a certain ability to flow, to be able to make full and perfect contact with a substrate. Dahlquist proposed the criterion that the storage modulus (G') for measurable quick tack must be below a certain fixed value (< 0.3 MPa).[35] A typical timescale for putting a PSA onto a surface is 1 s, so the relevant G' for a room temperature PSA is at 1 Hz for a temperature of 25 ºC. DMA measurements were performed using a parallel plate setup for the latices containing the different crosslinkers. The storage moduli are shown in Figure 3.
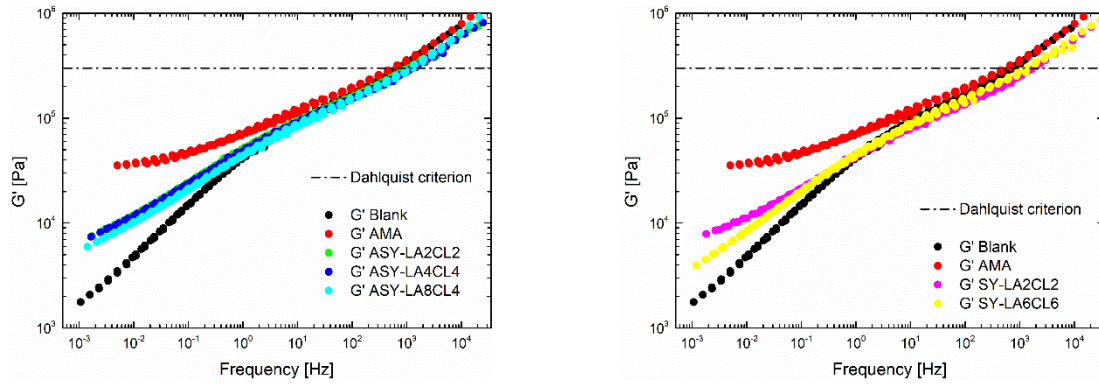
Figure 3: Storage moduli of the asymmetric (left) and symmetric (right) crosslinkers containing dried latices.

All the measured samples satisfied the Dahlquist criterion showing storage moduli values below 0.3 MPa at a frequency of 1 Hz. The AMA sample was the only one reaching a plateau between 10^4 and 10^5 Pa at low frequencies. On the other hand, the blank sample showed liquid like behaviour. The storage moduli of the samples containing oligoester crosslinkers were in between the AMA and the blank sample indicating a lower crosslinking density than the AMA latex in good agreement with the microstructure measured above (the storage moduli were higher for the samples containing the shorter oligoester crosslinkers). In the storage modulus, it can be observed that the most crosslinked system was the only one reaching a plateau and showing rubbery like performance. Furthermore, the ratio of tan(δ)/G' is related to the energy dissipation at the interface between adhesive and substrate. An increase in the viscous modulus with respect to the elastic modulus leads to an increase in resistance to the detachment. Values above 5 MPa^{-1} are recommended for steel substrates.[36] The tan(δ)/G' of the samples containing the different crosslinkers are plotted in Figure 4.
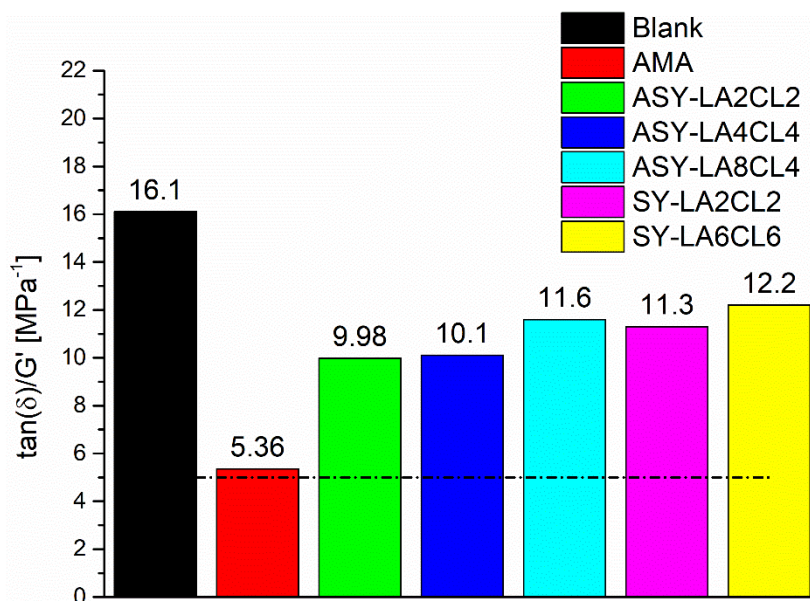
Figure 4: tan(δ)/g' for the polymers containing different crosslinkers at a frequency of 1 Hz and temperature of 25 ºC.

The AMA sample showed a value slightly above 5 MPa^{-1} for tan(δ)/G', whereas the blank showed a value of 16 MPa^{-1}. Values between 10 and 12 MPa^{-1} were calculated for the samples of the oligoester crosslinkers. Therefore, it can be concluded that the PSAs containing the oligoester crosslinkers are feasible to be used on steel substrates.

The performance of PSAs is characterized by adhesion and cohesion. Within this work, the adhesive performance of the non degradable PSAs (blank) together with the degradable ones are compared. 180º Peel resistance, loop-tack, shear resistance and SAFT measurements were carried out to prove the feasibility of the synthesized latices as PSA. A detailed description of the fundamentals and the experimental procedures used to measure these properties are presented in the Supporting Information. The results of these measurements are presented in Table 4.

Table 4: Adhesive properties of the latices: Average peel resistance, loop-tack, shear resistance and SAFT values.

Crosslinker	Peel [N/25mm]	Loop-tack [N/25mm]	Shear [min]	SAFT [ºC]
Blank	17.7 ± 1.9	35.2 ± 1.1	11 ± 3	39 ± 3
AMA	12.6 ± 1.2	13.5 ± 2.0	10000+	128 ± 34

ASY-LA2CL2	17.0 ± 1.1	16.4 ± 0.9	2714 ± 700	100 ± 15
ASY-LA4CL4	15.4 ± 2.1	16.3 ± 3.8	826 ± 110	95 ± 12
ASY-LA8CL4	20.4 ± 3.6	18.7 ± 1.7	413 ± 114	93 ± 8
SY-LA2CL2	12.7 ± 1.1	14.4 ± 0.6	5483 ± 1050	97 ± 8
SY-LA6CL6	21.0 ± 1.7	25.5 ± 2.6	140 ± 8	71 ± 4

Peel values between 12 N/25mm and 21 N/25mm were measured for the different samples. These are high values compared to commercially available duct tape (approximately 10 N/25mm[37]). The AMA and SY-LA2CL2 samples showed the lowest peel value (~13 N/25mm; they are the most crosslinked samples and with lower soluble fraction) while the highest peel values of 20 N/25mm and 21 N/25mm, respectively were observed for the sample of the longest asymmetric and symmetric crosslinker, these were even higher than the peel value of the blank sample (18 N/25mm). This could be due to the fact that peel resistance has a maximum in its dependency with the molar mass and crosslinking density[17], and likely these samples were closer to that value.

Tack on the other hand, showed the highest values for the lowest crosslinking density and/or molar mass and it decreases with increasing crosslinking density and/or molar mass. Thus, the blank sample showed by far the highest loop-tack value (35 N/25mm) followed by the SY-LA6CL6 and ASY-LA8CL4 samples (26 N/25mm and 19 N/25mm respectively) which had the lowest crosslinking density of the samples including crosslinkers. The other latices followed that trend, the lowest loop-tack values were observed for the AMA sample (14 N/25mm) and for the samples containing the two shortest asymmetric and symmetric crosslinker (16 N/25mm and 14 N/25mm, respectively). These are also high values compared to the commercial duct tape which shows a value of 7 N/25mm.[37]

Shear resistance and SAFT values also followed the trend according to the measured gel contents and molar mass distributions. The samples with the higher crosslinking density and higher molar masses (of the high molar mass mode) presented the higher times of failure. The lowest shear time of 11 minutes was observed for the blank sample and the highest of more than 10000 minutes for the AMA sample. Times of failure in between those two reference samples were observed for the asymmetric and symmetric oligoester crosslinkers containing samples. In the SAFT measurement, the blank sample failed at the lowest temperature of 39 ºC and the AMA sample at the highest temperature of

128 ºC. The longest symmetric one showed the lowest temperature of failure of 71 ºC. It is noticeable that the difference between the different crosslinkers is much more significant for the time of failure (shear resistance) than for the temperature of failure (SAFT).

Furthermore, probe tack measurements of the different crosslinkers containing PSAs were carried out on glass substrates and the stress strain curves are shown in Figure 5.
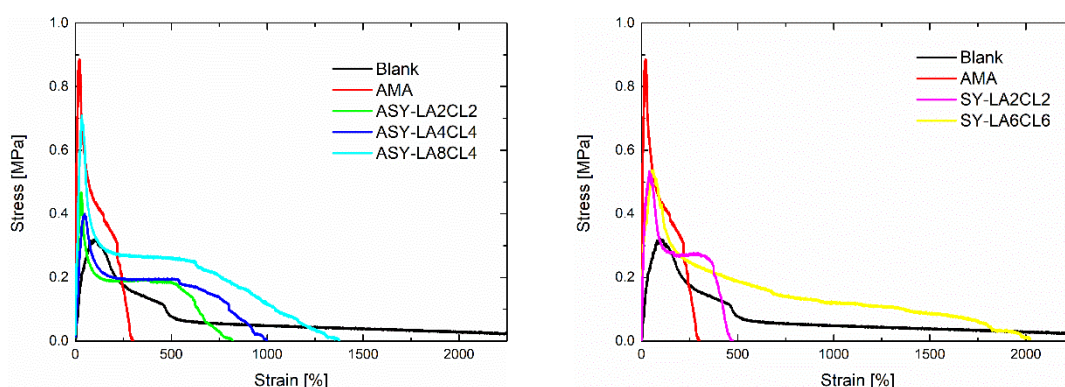

Figure 5: Stress strain curves obtained from probe tack measurements for the films of the latices with asymmetric (left) and symmetric (right) crosslinkers.

The curve measured for the AMA sample had no fibrillation plateau, indicating stiff behaviour, which is caused by its high degree of crosslinking (compare to Figure S1 I in the Supporting Information). The blank on the other hand behaved liquid-like (compare to Figure S1 III in the Supporting Information). The other samples with the oligoester crosslinkers, except for the SY-LA6CL6, which also behaved liquid-like and shows a strain up to 2000% before it broke, showed a fibrillation plateau (compare to Figure S1 II in the Supporting Information). The length of the plateau increased with increasing the oligoester crosslinker length. Moreover, the fibrillation plateaus of the samples with ASY-LA2CL2 and ASY-LA4CL4 had the same stress level of 0.2 MPa. The sample containing the longest asymmetric crosslinker ASY-LA8CL4 had the longest fibrillation plateau up to a strain of 1300%, and the higher stress level of 0.3 MPa. While the short symmetric crosslinker SY-LA2CL2 showed the shortest fibrillation plateau until a strain of almost 500% at a stress level of 0.3 MPa. The length of the fibrillation plateaus of the samples is in agreement with the microstructure measured for the synthesized pressure sensitive adhesives; the fibrillation plateau increases with a decrease in gel content and

decrease in molar masses (of the high molar mass peak of the bimodal distribution in Figure 2) up to a point in which no clear plateau, but liquid like behaviour (for the blank sample and the sample containing the longest symmetric oligoester crosslinker) is observed. The samples, except the longest asymmetric and symmetric crosslinker and the blank one, showed an abrupt fall of the stress at their maximum strain, which indicates an adhesive failure. This kind of error happens if the energy for crack propagation is lower than the energy needed to elongate the fibrils.[36,38] Overall the tested samples show similar performance in the probe tack test than non degradable waterborne PSAs (having the same comonomers of BA/MMA/AA) for which maximal strains in between 500% and 2000% were observed and which show a maximal stress of approximately 0.5 MPa and a fibrillation plateau at a stress level of 0.2 MPa (see Supporting Information Figure S2).[39]

The removability of the PSA's produced in this work depends on the degradation ability of the lactide/lactone oligoester crosslinkers. The degradation of polyesters and oligoesters by hydrolysis in either basic or acidic conditions has been described in the literature.[40] The mechanism and pH dependency of the degradation of PLA and PCL by hydrolysis was also investigated, and it was found that PLA degrades faster than PCL and that basic pH values lead to a higher rate of degradation than acidic pH values.[41,42] Therefore, basic conditions, similar to the pH of the washing solution used during the recycling of glass bottles, were chosen to assess the degradation of the adhesive films.

To proof that lactide and lactone moieties of the oligoester crosslinkers incorporated in polymer chains degrade under basic conditions, we first proved the concept in crosslinked copolymers synthesized by solution polymerization (see Supporting Information for the synthesis, degradation and characterization of the molar mass distribution before and after the alkali treatment). The alkali treatment clearly cleaved the crosslinking points, decreasing notably the molar mass of the polymer chains.

The same analysis could not be applied to the waterborne PSA films because they were not completely soluble in THF. Therefore, to monitor the degradation it was not possible to analyse the molar mass distribution before and after the degradation (note that the molar mass distributions presented in Figure 2 were obtained by dispersing the latices directly in THF). However, an indirect proof of the degradation (and also of the removability of the adhesive film) can be obtained by monitoring the probe tack of the films during the immersion in the alkali solution.

Therefore, probe tack measurements were performed before and after immersion at different times to assess the degradation of the films. The probe tack curves of the AMA sample (left) and of the ASY-LA8CL4 sample (right) after 0 min, 15 min and 30 min of immersion time are displayed in Figure 6.
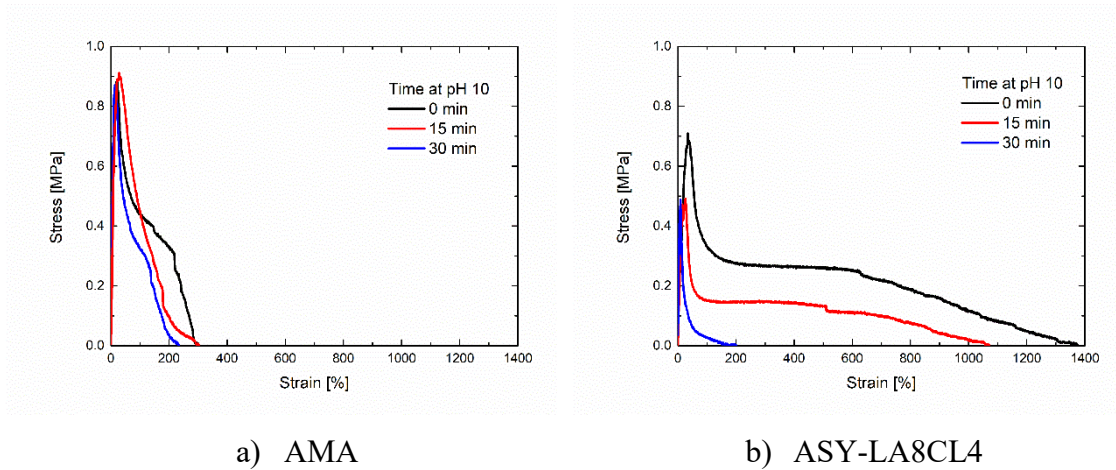

a) AMA   b) ASY-LA8CL4

Figure 6: a) Probe tack measurements of the AMA sample and **b)** of the sample with ASY-LA8CL4 crosslinker after immersion of the films on a glass substrate for certain times at basic pH.

The area below the probe tack curves of the AMA sample decreased slightly with the immersion time. However, the ASY-LA8CL4 sample showed a remarkable decrease in its area after 30 min of immersion, where the fibrillation plateau completely disappeared. The work of adhesion was calculated by integration of the probe tack curves for each sample at the different immersion times. Figure 7 shows the calculated work of adhesion normalized to the starting value at 0 min for the asymmetric (left) and symmetric (right) crosslinkers against the immersion times.
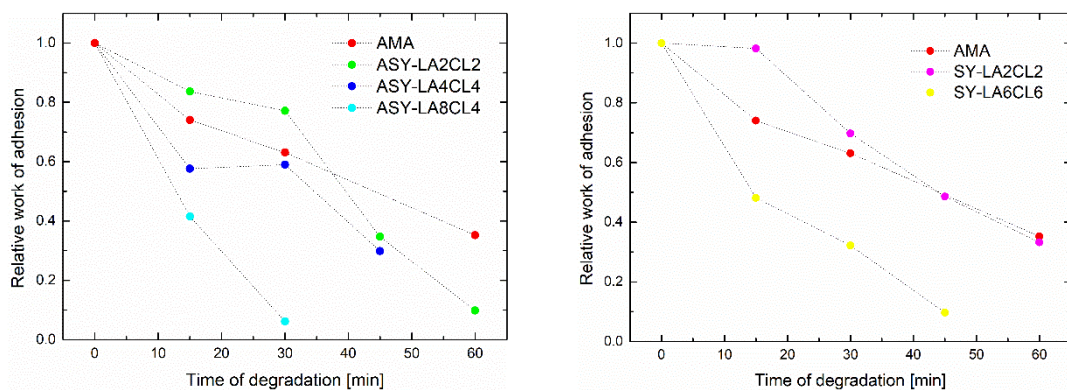

Figure 7: Relative work of adhesion calculated from the probe tack curves for the asymmetric (left) and symmetric (right) crosslinkers.

All of the samples showed a decrease in their relative work of adhesion with increasing time of immersion in the basic solution. Interestingly, the sample containing AMA also showed a substantial degradation up to 35% of its starting value. It has to be considered that the AMA crosslinker also contains an ester group which might also show degradation under these basic conditions. The samples of the shortest asymmetric and symmetric crosslinkers showed a similar degradation rate as the AMA sample. Nevertheless, the rate of degradation increases, increasing the length of the crosslinker, the longer the crosslinker the more ester groups in the molecule. The sample of ASY-LA8CL4 and SY-LA6CL6 showed a decrease in work of adhesion to 5% and 10% of the initial values in just 30 and 45 min, respectively.

Furthermore, as a proof of concept a film of the latex containing the ASY-LA8CL4 crosslinker, which is the sample showing the fastest rate of degradation in the probe tack measurements mentioned above, was cast onto a paper label for wine bottles. The label with the dried latex film was then attached to a glass bottle. This bottle and a commercial wine bottle with a label with a conventional non-degradable PSA were immersed into a basic potassium hydroxide solution with a pH of 10. After 24 hours of immersion the label and the PSA containing the oligoester crosslinker could be easily removed from the glass bottle whereas the label and the PSA of the commercial wine bottle could not be removed after 24 hours of immersion into the basic solution (Figures S4 and S5 and Videos S1 and S2 of the Supporting Information).

Conclusion

A novel approach to obtain waterborne degradable and easily removable PSAs and thus, a possibility to face one of the major issues of the label removal during the recycling of glass bottles has been presented in this work. Symmetric and asymmetric oligoester crosslinkers have been synthesized and used to replace the conventional crosslinker AMA in a waterborne PSA formulation. The oligoester crosslinkers did not show any significant effect on the seeded semibatch emulsion polymerization regarding the kinetics and particle evolution in comparison with the two reference samples (the blank and AMA). Soxhlet extraction and AF4/MALS/RI measurements proved that the oligoester crosslinkers worked as expected in this waterborne PSA formulation, obtaining high

molar masses and crosslinked samples. It is noteworthy that their efficiency is lower than that of AMA likely because of their limited solubility in the aqueous phase. In addition their efficiency decreases with chain-length. The adhesive properties using these novel crosslinkers are in between the performance of commercial waterborne PSAs, and the length of the oligoesters allows tuning the adhesive performance. Furthermore, the degradation of the PSA films was shown by probe tack measurements. The longest asymmetric and symmetric crosslinker showed a substantial decrease in their work of adhesion in such short times as 30 min and 45 min, respectively, when immersed in basic aqueous solution at room temperature. PSA labels were applied to a glass bottle and their degradability and easy removability was demonstrated as a further proof of concept. The simplicity to implement this kind of oligoester crosslinkers into (existing) waterborne PSA formulations and the fact that the incorporation of a low amount of oligoester crosslinkers as low as 0.2 mol% is sufficient to result in a PSA with promising degradation properties make the herein reported oligoester crosslinkers viable candidates for the production of removable PSAs. These removable PSA possess the potential to lead to a greener more sustainable way in the waste treatment, especially for the recycling of glass bottles.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgement

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