Supporting Information for:

Incorporation of novel degradable Oligoester Crosslinkers into a conventional Waterborne Pressure Sensitive Adhesive Formulation: Towards removable Adhesives

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Characterization of the pressure sensitive adhesives (PSAs)

The performance of PSAs is characterized by adhesion, required for bonding and debonding, and cohesion necessary against debonding. The character of PSAs is described by the special balance between these two properties. The adhesion of a PSA is described by peel and tack, whereas the cohesion of a PSA is characterised by shear resistance.^[1] In this section the basic principles for the characterization of PSAs are explained and a detailed description for the within this work conducted methods to measure PSA properties is provided.

Tests were performed at 23°C 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.HDPlus Texture Analyzer (Texture Technologies, Hamilton, MA, USA).

Peel Adhesion

In order to achieve peel adhesion the bonding stage must allow some dwell time. In this time the adhesive flows in absence of any externally applied forces to maximize the

contact with the substrate. Peel adhesion is one of the most important parameters to evaluate PSA properties.^[2] It is the force required to remove a PSA coated flexible material from a substrate under standard conditions (e. g. specific angle and rate). This force can be measured in different geometries. Common tests are carried out with a peeling angle of 90° or 180°. The determination of peel strength at an angle of 90° is advantageous for samples with low flexibility, which would suffer the risk of cracking, breaking or delamination at an angle of 180°.^[3] Peel measurements in this work were carried out at an angle of 180°.

180° Peel

The 180° Peel strength test was performed according to ASTM-D3330. PSA tapes with a width of 25 mm were applied to steel plates. Pressure was applied by rolling a 2 kg rubber coated weight 4 times over the steel plate. The applied tapes were left to dwell for 10 min. The tapes were then peeled off at a crosshead speed of 5 mm/sec. The average value of peel strength in N/25mm was obtained for peeling 6 cm of the tape specimens.

Tack tests

Tack is the resistance of an adhesive film to detachment from a substrate. It measures the ability to form an instant bond (no dwell time on the contrary to the peel test) when brought into low pressure contact with a substrate. The American Society for Testing and Materials defines tack as the force required to separate an adherent and an adhesive at the interface, shortly after they were brought rapidly into contact under a light pressure of short duration (ASTM-1878-6). Tack can be measured quantitatively by a loop tack tester or by contact mechanics such as probe tack tests.^[1]

Loop tack

Loop tack defines the force that is required to separate a loop of material at a specific speed from a specific area of a standard surface with which it was brought into contact with for a certain contact time (without applying a significant pressure).^[1]

The loop tack test was carried out according to ASTM-D6195. PSA tapes with a length of 100 mm and a width of 25 mm were attached in the shape of a loop with the PSA facing to the outside of the loop to the upper grip of the equipment. The loop was then moved downwards with the speed of 0.100 mm/s until it came into full contact with a stainless steel plate (width 25 mm) in an area of 25 mm x 25 mm. After a contact time of 0.1 s the loop was moved upwards with a speed of 0.055 mm/s. The force required to peel off the loop was measured in N/25mm and the average value was reported.

Probe tack

The probe tack test is a powerful tool to gain information about the debonding mechanism of an adhesive. The parameters influencing the results of the probe tack test are the rheological properties of the adhesive layer and the nature of its interaction with the surfaces of the substrate and the probe.^[4] The adhesive performance is characterized by three parameters obtained from the force-displacement curve: the maximal nominal stress ($^{\sigma}max$), the strain at break ($^{\epsilon}max$) and the adhesion energy, which is defined as the area below the stress strain curve from the probe tack experiment (equation S1).

$$W_{adh} = h_0 \int_0^{\epsilon max} \sigma(\epsilon) d\epsilon$$
 (S1)

Also, the shape of the stress strain curve provides information of the nature of the adhesive. Four different types of probe tack curves were distinguished for different adhesives (Figure S1). The first type of these curves is defined by a sharp maximum in stress at relatively low strains and a low total area below the curve (Figure S1, I), this kind of behaviour is usually related to samples with high glass transition temperatures or/and high crosslinking density or/and high molar mass. The other extreme type is liquid like behaviour as shown in Figure S1, III. This type of curves is observed for adhesives with a low glass transition temperature or/and low crosslinking density or/and low molar mass. This kind of behaviour is dictated by the viscous flow of the adhesive, leading to a breakage within the adhesive itself, leading to a cohesive failure, which can be observed by residues of the adhesive, which stay at the probe after the breakage. Most adhesives

show a behaviour in between these two extremes (Figure S1, II). In this case, the curves are defined by reaching a sharp peak of the maximum of the stress, followed by a pronounced shoulder and finally reaching zero. In this case, the detachment happens between the probe and the adhesive layer, the so called adhesive failure. For this kind of behaviour the adhesive completely debonds from the probe so that no macroscopic residues are left over at the probe. This type of curve represents a typical stress-strain curve for a probe tack experiment with an adhesive. Within this curve, it is possible to distinguish between different stages of the debonding mechanism. At first, in the linear elastic domain, the adhesive layer is homogenously deformed, then cavities start to form in the adhesive film, the deformation is becoming non-linear, inhomogeneous and non-reversible. The stress then stabilizes at a lower, nearly constant value, which is caused by the formation (from the walls between the cavities) and elongation of fibrils. The stress reaches zero when the fibrils break.^[5]



Figure S1: Different stress-strain curves for the probe tack experiment. I) Brittle failure, II) adhesive debonding with hardening in the case of II b), III) cohesive debonding of a liquid like behaving adhesive.^[5]

The probe tack tests were performed on glass plates according to ASTM-D2979. Films were casted from the latices and dried for 12 h before the measurements were carried out. A 1 inch stainless steel ball was moved downwards to the film with a speed of 0.1 mm/s and brought into contact with the PSA film for a contact time of 1 s. Thereafter, the stainless steel ball was moved upwards at a speed of 0.055 mm/s until either a cohesive

or adhesive error was observed, so that the probe was completely separated from the PSA film.

Figure S2 shows probe tack curves for non degradable waterborne PSA with a similar formulation as the PSAs synthesized in this work, also with the monomers BA/MMA/AA in the same composition as for the PSA synthesized within this work but without using any kind of crosslinker or chain transfer agent. Each of the curves represent a latex following this formulation but different surfactants are used. The sample Dowfax-3 represents a latex using the surfactant Dowfax 2A1 as it is also used within this work.



Figure S2: Stress-strain curves of the probe tack curves obtained for a conventional non degradable waterborne PSA formulations with the monomers BA/MMA/AA. The difference between the curves being the used surfactants. Reprinted from *Int. J. Adhes. Adhes.* with permission from Elsevier.^[6]

Shear and SAFT tests

Shear resistance is measured as a force required to pull the pressure sensitive material parallel to the surface it was attached to with a definite pressure and gives information

about the cohesive performance of a PSA. Usually the holding time is measured under standard conditions. The holding power is basically a viscosity effect. The adhesive should not break under debonding forces (mainly shear and peel forces). This requirement is inverse to Dahlquist's criterion which states that the storage modulus has to be below a certain value for measurable quick tack.^[1]

Shear tests were carried out on steel plates using SAFT equipment (Sneep industries) according to ASTM-D3654. PSA tapes were attached within an area of 25 mm x 25 mm of the steel plate. Pressure was applied by rolling 1 kg weight 4 times over the steel plate attached to the PSA tape. The attached PSA tapes were left for 10 min to dwell. A weight of 1 kg was then attached to the PSA tape. The steel plates with the attached tapes were held by a test stand at an angle of 1° relative to the vertical and at a temperature of 23 °C. The time from the attachment of the weight until the complete separation of the tape from the steel plate is recorded and reported as time of failure, which is an indication for the shear strength of the PSA tapes. The SAFT tests were prepared similarly. The difference being that a temperature ramp from 23 °C to 200 °C with a rate of 1 °C/min was applied as soon as the weight was attached. For this test, the temperature of failure is reported.

Analysis of synthesized oligoester crosslinkers by proton nuclear magnetic resonance spectroscopy (NMR)

Proton NMR was carried out to characterize the synthesized oligoester crosslinkers. The spectrum of one asymmetric oligoester crosslinker (ASY-LA4CL4) is shown in Figure S2 and the spectrum of one symmetric oligoester crosslinkers is shown in Figure S3 for each of them the protons of the molecules are assigned to the signals of the spectra.





Figure S2: ¹H-NMR spectrum of the synthesized ASY-LA4CL4 oligoester crosslinker with assignment of the signals.

The number of lactic acid (n(LA)) and ε -caprolactone (n(CL)) units for each of the asymmetric oligoester crosslinkers was calculated as shown in equation S2a and S2b. In which I(a) is the integral of proton a, I(n) is the integral of proton n and I(h) is the integral of proton h.

$$n(LA) = \frac{I(n)}{I(a)}$$
(S2a)

$$n(CL) = \frac{I(h)}{I(a) \cdot 2}$$
(S2b)





Figure S3: ¹H-NMR spectrum of the synthesized SY-LA6CL6 oligoester crosslinker with assignment of the signals.

The number of lactic acid (n(LA)) and ε -caprolactone (n(CL)) units for each of the symmetric oligoester crosslinkers was calculated as shown in equation S3a and S3b. In which I(p) is the integral of proton p, I(j) is the integral of proton j and I(d) is the integral of proton d.

$$n(LA) = \frac{I(j) \cdot 2}{I(p)}$$
(S3a)

$$n(CL) = \frac{I(d)}{I(p)}$$
(S3b)

Following these equations (Equation S2a, S2b, S3a and S3b) it is possible to calculate the molar masses of each of the crosslinker through the number of units and their molar masses.

Degradation of PSA copolymers synthesized by solution polymerization

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.

The monomers BA/MMA/AA (in the ratio 89.1/9.9/1) were polymerized in a solution polymerization with a solid content of 30% in toluene, using 1 mol% of the oligoester crosslinkers. 5 wbm% of AIBN were added after the polymerization temperature was reached. The solution polymerizations were carried out for 4 hours at 70 °C and under nitrogen atmosphere.

The oligoester crosslinkers ASY-LA4CL4 and SY-LA6CL6 were used in a solution polymerization with the monomers BA/MMA/AA (89.1/9.9/1) and compared to the blank (without using a crosslinker). The dried polymer was immersed for 24 h in a potassium hydroxide solution to degrade. The molar mass distributions measured by Gel Permeation Chromatography (GPC) before and after degradation are shown in Figure S4.



Figure S4: Molar mass distribution of the polymers obtained from solution polymerization before (straight line) and after degradation (dashed line) at basic pH.

The molar mass distribution of the polymers with oligoester crosslinkers is broader compared to the molar mass distribution of the blank polymer clearly showing the crosslinking reactions in the presence of the oligoester crosslinkers. The distribution of the blank after immersing it into a basic solution had a negligible effect on the molar mass distribution, whereas the distribution of the oligoester containing polymers gets much narrower and almost like the blank after the degradation. The weight average molar masses and the dispersity index of the polymers obtained by solution polymerization are displayed in Table S1.

	M _W [g/mol]	PDI
Blank	80800	2.0
Blank degraded	65000	2.2
ASY-LA4CL4	297600	4.7
ASY-LA4CL4 degraded	96000	2.5
SY-LA6CL6	375400	6.4
SY-LA6CL6 degraded	108000	2.5

Table S1: Weight average molar mass and dispersity index of the polymers from solution polymerization before and after degradation at basic pH.

The weight-average molar mass of the blank decreases around 20% after degradation, whereas the weight average molar mass of the polymers with the synthesized oligoester crosslinkers is around one third of the initial value after degradation. Furthermore, the polydispersity of the polymer including the asymmetric oligoester crosslinker decreases from 4.7 to 2.5 and of the polymer including the symmetric crosslinker from 6.4 to 2.5. On the other hand the blank polymer shows a slight increase in dispersity from 2.0 to 2.2 after degradation. These results prove that the synthesized oligoester crosslinkers are able to act as crosslinkers in a co-polymerization with acrylate monomers and that the crosslinks are degradable in basic media.

PSA synthesis by seeded semibatch emulsion polymerization

The PSAs were produced in two step seeded emulsion polymerization procedure. First, the seed was produced following the recipe shown in Table S2.

Ingredient	Amount [g]	Percentage [wbm%]		
BA	185.18	89.1		
MMA	20.67	9.9		
AA	2.09	1.0		
Dowfax 2A1	11.53	2.5		
Water	353.06	170.0		
Ammonia	8.36	4.0		
KPS	0.52	0.25		

Table S2: Formulation of the synthesized by semibatch emulsion polymerization.

Reaction temperature: 80 °C; Agitation: 200 rpm.

In the second step the seed was grown in a semibatch emulsion polymerization process following the recipe shown in Table S3.

Ingredient	Amount [g]	Percentage [wbm%]
Seed	18.00	9.0
BA	178.80	89.1
MMA	19.90	9.9
AA	2.02	1.0
Dowfax 2A1	2.78	0.6
Water	182.50	58.9
Crosslinker*	0.46-5.61	0.2 mol%
t-DDM	0.30	0.15
KPS	0.49	0.25
Sodium bicarbonate	0.49	0.25

Table S3: Formulation of the seeded semibatch emulsion polymerizations.

*The percentage of the crosslinkers is reported in mol% (based on the monomers) instead of wbm% due to the different molar masses of the used crosslinkers.

Reaction temperature: 75 °C; Agitation: 200 rpm.

Removability test of PSA labels from glass bottles

The glass bottles and their labels were immersed into a basic aqueous solution for 24 h and it was tried to peel the labels off from the bottles by hand. The label from the commercial wine bottle could not be removed (Figure S5 and Video S1).



Figure S5: Commercial wine bottle with commercial label and PSA after immersion into basic aqueous solution for 24 h.

Degradable	crosslinking	in	waterborne	PSAs	VS1	Video S1
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On the other hand, the label which was attached with the oligoester crosslinker (ASY-LA8CL4) containing latex could be removed easily after an immersion into the basic aqueous solution for 24 h (Figure S6 and Video S2).



Figure S6: Paper label attached to a glass bottle with PSA which includes a synthesized oligoester crosslinker (ASY-LA8CL4) after immersion into a basic aqueous solution for 24 h.

References

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