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# Secondary dispersion-based reactive pressure-sensitive adhesives with improved tack

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**ABSTRACT:** Reactive pressure-sensitive adhesives (PSA) have to meet the requirements for sufficient tack prior to crosslinking but also high shear after crosslinking. This article examines the use of secondary acrylic dispersions with reactive groups and epoxy resin dispersions for such PSA. Long-term stable secondary PSA dispersions with high tack after film formation were obtained. Tack was dependent on the amount of carboxylic acid groups in the polymer as well as the base used for partial neutralization of the solvent-borne copolymers. Reactive PSA were prepared by mixing a secondary dispersion with high amounts of carboxylic acid groups with an epoxy resin dispersion providing no tack. Variation of mixing ratio gave reactive PSA with sufficient tack, peel, and shear prior to crosslinking. Crosslinking of these reactive PSA at elevated temperatures led to high shear which was limited by incomplete molecular mixing of both phases. © 2018 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2018**, *135*, 46315.

**KEYWORDS:** crosslinking; emulsion polymerization; pressure sensitive adhesives; radical polymerization; resins

## INTRODUCTION

Aqueous acrylic dispersions have received much attention in recent years due to low VOC and thus environmental friendliness.<sup>1–3</sup> Acrylic dispersions are prepared mainly by two synthesis routes namely the acetone process and emulsion polymerization.<sup>4–6</sup> These dispersions are used for a wide range of pressure-sensitive adhesives (PSA) and coatings applications and tend to replace solvent-borne systems. Emulsion polymerization of acrylic monomers leads to primary dispersions in which the polymerization and formation of the dispersion takes place at the same time.<sup>7</sup> The acetone process consists of the consecutive preparation of a solvent-borne acrylic copolymer with carboxylic acid groups and formation of a secondary dispersion upon partial neutralization, addition of water as well as removal of solvent.<sup>8,9</sup> Influences on the particle size distributions are well known for the preparation of polyurethane dispersions also prepared by the acetone process.<sup>10–13</sup> In contrast to primary dispersions no to little amounts of surfactants are necessary for the preparation of secondary dispersions because of self-emulsifying properties of the carboxylate anions at the polymer chains formed during neutralization. A considerable amount of literature has been published on different synthesis routes of

secondary dispersions for coating applications.<sup>14–20</sup> These routes differ mainly on the nature of ionic groups originating from different functional groups such as carboxyl, hydroxyl, and epoxy groups. Polymer dispersions synthesized by emulsion polymerization and the acetone process lead to polymer films with completely different mechanical properties. Side reactions during emulsion polymerization such as chain transfer reactions give elastomeric high molecular weight particles while solution polymerization lead to thermoplastic low molecular weight polymers and hence thermoplastic particles of the secondary dispersions.<sup>21–23</sup> Crosslinking of the elastomeric particles influence the performance of the final polymer film by limited interdiffusion due to formation of discontinuous networks.<sup>24,25</sup> Previous research has found formation of continuous networks for elastomeric particles upon optimization of polymer architecture and crosslinking.<sup>26–28</sup> In contrast to emulsion based polymers solvent-borne acrylic polymers always give continuous networks leading to improved shear.<sup>29,30</sup> The acetone process transfers continuous network forming solvent-borne acrylic copolymers to aqueous secondary dispersions with low VOC. Yet, primary acrylic dispersions have a pivotal role in PSA applications while secondary acrylic dispersions are mainly used for coating applications. So far, very little attention has been paid to the role of

secondary acrylic dispersions for PSA. On the other hand, secondary acrylic dispersions provide high tack and might be promising for increasing tack of PSA formulations. Because of their thermoplastic nature, solvent-borne acrylic polymers need to be crosslinked prior use as PSA for improvement of shear resistance.<sup>31–34</sup> Previous research of primary dispersions has established multiple ways for increasing shear of PSA by crosslinking pendant reactive groups.<sup>35,36</sup> Carboxylic acid and epoxy groups have been the subject of many studies regarding crosslinking at ambient to medium temperatures.<sup>37–42</sup> Further methods include variation of pH of primary dispersions containing carboxylic acid groups leading to changes of intermolecular interactions between polymer chains.<sup>43</sup> Dual crosslinkable adhesives based on blends of acrylic monomers with carboxylic acid groups and epoxy resins by subsequent exposure of UV radiation and thermal treatment have been also established.<sup>44</sup> Blends of primary acrylic dispersions and epoxy resin dispersions are also known in literature.<sup>45,46</sup> Furthermore, approaches include the emulsification of epoxy resins during the acetone process by self-emulsifying acrylic resins.<sup>19,47–49</sup> Recent work dealt with the preparation of core-shell particles by using epoxy resin dispersions as seed in emulsion polymerization of methyl methacrylate and methacrylic acid (MAA).<sup>50</sup> Additionally, three layer core shell particles have been also prepared by seeded emulsion polymerization without acrylic and MAA.<sup>51</sup> Miniemulsion polymerization of acrylic monomers and epoxy resins are also well known in literature.<sup>41,52</sup> However, the main focus of the abovementioned methods was to obtain specific particle morphologies with no post-crosslinking taking place. The abovementioned crosslinking reactions known for reactive compositions containing acrylic polymers might be transferred to secondary dispersions possibly leading to structural adhesives by post-crosslinking.

This work considered the use of a secondary acrylic dispersion with high contents of carboxylic acid groups and solid epoxy resin dispersion for reactive PSA. The secondary dispersion provided tack for the reactive PSA and led to sufficient tack prior crosslinking for joining and fixation of parts as well as improved shear after crosslinking by thermal treatment. On a long term view the presented examinations should lead to PSA for quick assembling processes which can be cured in a following step to form a structural adhesive. This would lead to an improved productivity in adhesive bonding.

## EXPERIMENTAL

### Materials

2-ethylhexylacrylate (2-EHA, >99% purity, BASF, Ludwigshafen, Germany), acrylic acid (AA, >99% purity, BASF, Ludwigshafen, Germany), azobisisobutyronitrile (AIBN, >98% purity, Akzo-Nobel Functional Chemicals, Arnhem, the Netherlands), dimethylethanolamine (DMEA, >99% purity, GB Chemie, Messel, Germany), sodium hydroxide (>98%, BCD Chemie, Hamburg, Germany), methyl ethyl ketone (MEK, >99% purity, BCD Chemie, Hamburg, Germany), EPI-REZ Resin EP6006-W-68 (epoxidized ortho-cresylic novolac with an average functionality of six, Hexion, Columbus, Ohio), Rheovis AS 1130 (BASF, Ludwigshafen, Germany) and deionized water were used for the preparation of reactive PSA and were used as supplied.

**Table I.** Solution Polymerization and Secondary Dispersion Preparation for the PSA with 10 wt % AA in the Polymer

Step	Component	Amount (g)
1	MEK	300
2	MEK	50
2	AIBN	5
2	2-EHA	405
2	AA	45
3	MEK	80
4	MEK	20
4	AIBN	1
5	DMEA/water (1:1 by weight)	30.5
6	Water	820

### Solution Polymerization and Preparation of a Secondary Dispersion

The solvent-borne copolymer was prepared by solution polymerization, which was carried out in a 2 L glass jacket reactor vessel fitted with a condenser, mechanical stirrer, and platinum resistance thermometer. Table I shows the formulation of a solvent-borne copolymer and a secondary dispersion made of it. For the preparation of a solvent-borne copolymer MEK was charged into the reactor and heated to 80 °C (step 1). Then, a mixture of monomers (AA, 2-EHA), solvent (MEK) and initiator (AIBN) was fed to the reactor over 2 h (step 2). Additional MEK was added to give a solution with sufficiently low viscosity (step 3). Afterwards, the solution was kept at 80 °C for 3 h before the shotwise addition of an AIBN solution (step 4). The solution was held at 80 °C for 3 h and eventually cooled down to room temperature. A small amount of solution (80 g) was removed for further characterization. For the preparation of the secondary dispersion, a DMEA/water mixture was added to the solution and stirred for 0.5 h (step 5). Then, water was fed to the reactor over 1 h (step 6) and the mixture was stirred for 1.5 h. Finally, the solvent was removed under reduced pressure (40 °C, 65 mbar) until the solid content exceeded the theoretical solid content of 33%. For examination of tack the concentration of AA for solvent-borne copolymers was varied from 10 to 25 wt % with respect to the monomer mixture. The final solid content of all shown solvent-borne copolymers was kept constant at 50% while the final solid content of the secondary dispersion was 36%.

### Characterization

The particle size distributions were measured via dynamic light scattering (DLS) with Zetasizer Nano-S (Malvern Instruments, Malvern, UK). All samples were diluted to about 0.5% and were measured at 25 °C. The reported diameters were an average of 12 consecutive measurements. For time dependent measurements the analysis was repeated 6 times.

The probe-tack tests were performed with Texture Analyser TA.XTplus (Stable Micro Systems, Godalming, UK) with a modified version of the Avery Adhesive test. The spherical probe (1 in) was made of stainless steel. All solvent-borne copolymers and dispersions were cast onto glass plates (wet thickness 80

$\mu\text{m}$ ) and dried at  $75^\circ\text{C}$  for 0.5 h. In general, Rheovis AS 1130 was added to all examined reactive dispersions for adjustment of viscosity (1.5 wt % on total formulation). Probe-tack tests were carried out with a contact force of 0.1 N and a contact time of 10 s. The probe rate was varied from 10 to 1000  $\mu\text{m/s}$ .

ATR-IR spectra were recorded with an Equinox 55 spectrometer (Bruker Optics, Ettlingen, Germany) equipped with a Golden Gate ATR Unit (Specac, Fort Washington, Pennsylvania). All spectra were recorded with 32 scans and a resolution of  $4\text{ cm}^{-1}$ . After baseline correction ATR-IR spectra were normalized by a peak area from  $3027$  to  $2781\text{ cm}^{-1}$  (alkane region). Integrals were determined from  $1610$  to  $1515\text{ cm}^{-1}$  (carboxylate group). The PSA were cast onto a glass plate with a wet thickness of  $80\text{ }\mu\text{m}$  and dried for 0.5 h at  $75^\circ\text{C}$ .

DSC measurements were performed with a Discovery DSC (TA Instruments, New Castle, Delaware). The sample was first cooled down to  $-70^\circ\text{C}$  with  $10\text{ K/min}$ . Then, the sample was heated to  $220^\circ\text{C}$  at a heating rate of  $10\text{ K/min}$ .

For peel and shear all PSA were cast onto a poly(ethylene terephthalate) sheet (PET,  $50\text{ }\mu\text{m}$  Müller Ahlhorn, Ahlhorn, Germany) with a wet thickness of  $80\text{ }\mu\text{m}$  and dried at  $75^\circ\text{C}$  for 0.5 h. The width of the final PET strips was  $25\text{ mm}$ . Peel and shear was determined within 72 h and determined according to DIN EN 1939 (test rate:  $300\text{ mm/s}$ ) and DIN EN 1943 (test weight:  $1\text{ kg}$ ). Measurements were performed with a Zwick Roell Z10 (Zwick, Ulm, Germany) and Shear Tester RT-10 (ChemInstruments, Fairfield, Ohio).

The weight average molecular weight was determined by gel permeation chromatography (GPC) with an Agilent Technologies 1260 Infinity (PSS Polymer Standard Service, Mainz, Germany) equipped with a refractive index detector. Samples were dissolved in tetrahydrofuran containing 0.5 wt % trifluoroacetic acid. Polystyrene was used as a standard. The precolumn was a PSS SDV  $5\text{ }\mu\text{m}$  Guard ( $8 \times 50\text{ mm}$ ), the main columns were PSS SVD  $5\text{ }\mu\text{m}$  100 ( $8 \times 300\text{ mm}$ ), PSS SVD  $5\text{ }\mu\text{m}$  1000 ( $8 \times 300\text{ mm}$ ), PSS SVD  $5\text{ }\mu\text{m}$   $10^5$  ( $8 \times 300\text{ mm}$ ) and PSS SVD  $5\text{ }\mu\text{m}$   $10^6$  ( $8 \times 300\text{ mm}$ ).

Specimens for dynamical mechanical analysis (DMA) were prepared by casting a reactive PSA dispersion onto release paper with a wet thickness of  $250\text{ }\mu\text{m}$ . The films were dried at  $75^\circ\text{C}$  for 0.5 h and crosslinked at  $115^\circ\text{C}$  for 1.5 h. DMA was performed with a DMA 2980 Dynamic Mechanical Analyzer (TA Instruments, New Castle, Delaware) and specimens ( $9 \times 5 \times 0.05\text{ mm}$ ) were examined with a strain of about 0.05% and a frequency of  $1\text{ Hz}$ . The sample was cooled down to  $-150^\circ\text{C}$  and heated to  $150^\circ\text{C}$  at a heating rate of  $2\text{ K/min}$ .

Lap-shear samples were prepared with aluminum substrates (AlMg3 alloy). Reactive PSA dispersions were cast onto two substrates (wet thickness  $150\text{ }\mu\text{m}$ ) and dried at  $75^\circ\text{C}$  for 0.5 h. Both substrates were joined and fixed (overlapping:  $25 \times 13\text{ mm}$ ). Then, the adhesive was cured at  $115^\circ\text{C}$  for 1.5 h.

Centrifugation was performed with a Heraeus Megafuge 16R Centrifuge (Thermo Fisher Scientific, Waltham, Massachusetts). Samples were centrifugated two times consecutively at  $17,000g$  and  $4^\circ\text{C}$  for 10 min.

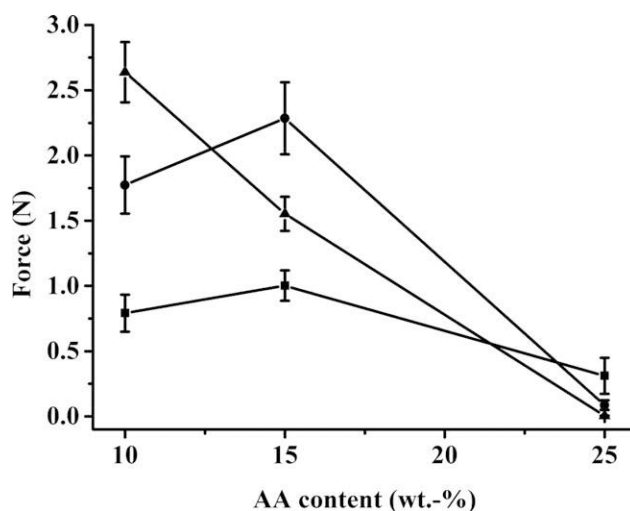
The solid content was determined with a Sartorius MA 45 (Sartorius, Göttingen, Germany). The samples were heated to  $125^\circ\text{C}$  and the temperature was kept constant until the end of the measurement.

Scanning electron microscopy (SEM) was performed with a Leo Gemini 1530 (Zeiss, Jena, Germany). Fracture surfaces of DMA specimens were prepared by fracture in liquid nitrogen. All samples were sputtered with palladium and platinum in advance of examination.

## RESULTS AND DISCUSSION

### Influence of Acrylic Acid on the Molecular Weight Distribution and Tack of Solvent-Borne PSA

Solvent-borne copolymers based on 2-EHA and AA were prepared with different contents of AA. For a high tack monomers resulting to polymers with low  $T_g$  are required. Typically 2-EHA or butylacrylate are therefore the most common monomers for acrylate-based PSA. Due to its lower  $T_g$  2-EHA was selected for the work presented here. It was apparent beforehand that increasing amounts of AA would lead to decreasing probe-tack due to increasing  $T_g$  as well as enhanced interactions by hydrogen bonds between polymer chains.<sup>53</sup> However, it is known from literature that in contrast to primary dispersions a distinct amount of AA is required for the preparation of secondary dispersions.<sup>1,8,9</sup> Therefore, the main purpose of this examination was to achieve PSA with high contents of AA and sufficient tack. Figure 1 shows the dependence of the probe-tack of solvent-borne copolymers containing 10, 15, and 25 wt % AA. Polymer films containing 10 and 15 wt % AA gave increasing probe-tack values with increasing probe rates and showed cohesive failures in most cases. Yet, a transition from cohesive to adhesive failure occurred at  $1000\text{ }\mu\text{m/s}$  for copolymers containing 15 wt % AA indicating loss of polymer chain mobility which is reflected in  $T_g$  changes as well (Table II). On the other hand, higher contents of AA (25 wt %) led to an inevitable loss of probe-tack with adhesive failure at all shown probe rates.



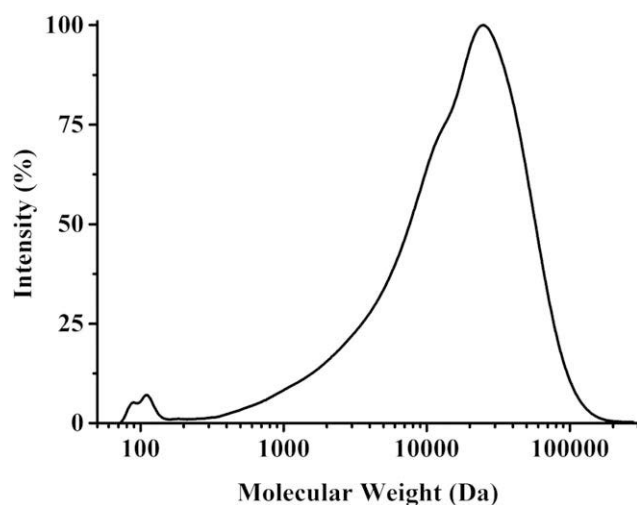
**Figure 1.** Dependence of probe-tack for PSA films on the AA content (10, 15, 25 wt %) for different probe rates (■:  $10\text{ }\mu\text{m/s}$ ; ●:  $100\text{ }\mu\text{m/s}$ ; ▲:  $1000\text{ }\mu\text{m/s}$ ). The PSA consisted of a solvent-borne polyacrylate with 2-EHA and AA as monomers.

**Table II.** Number Weight Average Molecular Weight ( $M_N$ ), Weight Average Molecular Weight- ( $M_W$ ), Polydispersity Indices (PDI), Theoretical  $T_g$  ( $T_{g,fox}$ ), and Experimental  $T_g$  ( $T_{g,exp}$ ) of Solvent-Borne Copolymers for Different Contents of AA (10, 15, 25 wt %)

AA content (wt %)	$M_N$ (Da)	$M_W$ (Da)	PDI	$T_{g,fox}$ (°C)	$T_{g,exp}$ (°C)
10	3655	23,950	6.6	-48.3	-51.4
15	7690	28,320	3.7	-43.1	-38.1
25	7625	31,960	4.2	-31.9	10.9

The PSA consisted of a solvent borne polyacrylate with 2-EHA and AA as monomers.

These trends and changes in probe-tack behavior are in agreement with existing results for PSA containing different amounts of AA.<sup>53</sup> Because of consistent cohesive failures and rising probe-tack values at higher probe rates the PSA containing 10 wt % AA fulfilled the criteria of sufficiently high amount of AA as well as sufficient tack and was used in further experiments. In addition, changes in molecular weight distributions caused by changes in monomer composition and homopolymerization might affect the examined PSA by influencing molecular entanglement.<sup>29,54</sup> Thus, molecular weight distributions were determined by GPC measurements for all solvent-borne copolymers as displayed in Table II and one exemplary distribution in Figure 2. As can be seen in the Table and Figure, all distributions and polydispersity indices were close to another ranging from 24,000 to 32,000 g/mol and 3.7 to 6.6 indicating copolymers of 2-EHA and AA owing to the absence of homopolymerization. However, comparison of each experimental  $T_g$  with the theoretical  $T_g$  according to the fox-equation reveals increasing differences with higher contents of AA (Table II).<sup>1</sup> Calculation of theoretical  $T_g$  was performed with  $T_g$  taken from literature for homopolymers of 2-EHA (-58 °C) and AA (106 °C).<sup>1</sup> The solvent-borne copolymer containing 10 wt % AA gives a similar  $T_g$  (-51.4 °C) to the theoretical  $T_g$  (-48.3 °C) while 25 wt %

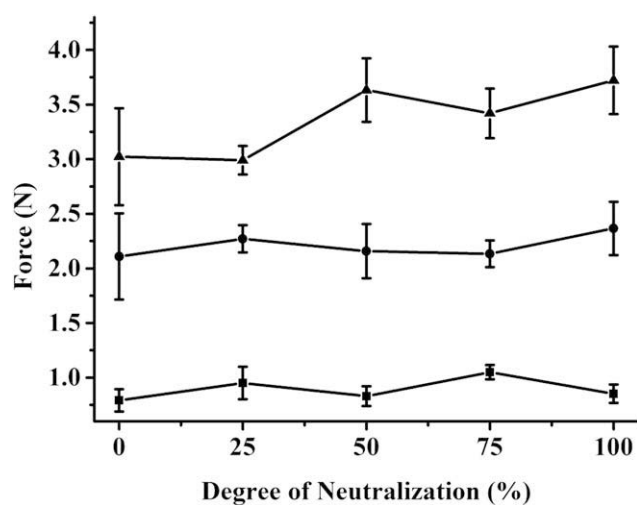


**Figure 2.** Molecular weight distribution obtained by GPC of a solvent borne acrylic copolymer with 10 wt % AA. The PSA consisted of a solvent-borne polyacrylate with 2-EHA and AA as monomers.

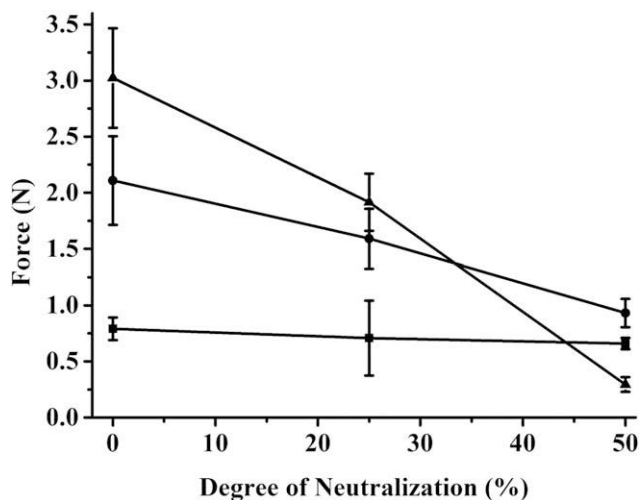
AA leads to noticeable different  $T_g$  (10.9 °C) to the theoretical  $T_g$  (-31.9 °C). This behavior shows a clear tendency towards hydrogen bonds which lower the polymer mobility and increase the  $T_g$  of the examined solvent-borne PSA thus suggesting theoretical  $T_g$  well under the experimental  $T_g$  for PSA with 15 and 25 wt % AA. Formation of blocks along the polymer chains can be excluded also at higher contents of AA (15 and 25 wt %) as DSC shows only one glass transition typical for random copolymers (Figure S1). In addition <sup>1</sup>H-NMR reveals a similar spectrum as that of random copolymers of 2-EHA and AA known from the literature (Figure S2 and Table S1). Because of similar molecular weight distributions, all observed probe-tack behaviors were directly related to changes in  $T_g$  as well as changes in molecular interactions due to increasing hydrogen bonding between polymer chains.

### Influence of the Neutralization on Tack of Solvent-Borne Copolymers

In order to prepare acrylic secondary dispersions from solvent-borne copolymers they need to be neutralized before emulsification.<sup>8,9</sup> The type of base used influences the anion formation and thus the physical properties of the PSA.<sup>43</sup> This experiment focuses on the influence of one volatile base DMEA and one nonvolatile base sodium hydroxide (NaOH) on the probe-tack of PSA containing 10 wt % AA. Probe-tack values in Figure 3 suggest that different degrees of neutralization for DMEA containing samples have no influence on the probe-tack of PSA for all examined probe rates. On the contrary Figure 4 demonstrates that NaOH neutralized samples have different probe-tack at different degrees of neutralization and different probe rates. It can be observed that no change in probe-tack occurs at 10  $\mu\text{m/s}$  for all degrees of neutralization. However, higher probe rates led to a decrease of probe-tack with increasing degrees of neutralization indicating changes in rheological behavior. Apparently anion formation by addition of NaOH to a solvent-borne copolymer containing AA gives increasing cohesive strength which is known in literature for emulsion-based



**Figure 3.** Dependence of probe-tack for PSA films on the degree of neutralization with DMEA for different probe rates (■: 10  $\mu\text{m/s}$ ; ●: 100  $\mu\text{m/s}$ ; ▲: 1000  $\mu\text{m/s}$ ). The PSA consisted of a solvent borne poly(2-EHA) containing 10 wt % AA.



**Figure 4.** Dependence of probe-tack for PSA films on the degree of neutralization with NaOH for different probe rates (■: 10  $\mu\text{m/s}$ ; ●: 100  $\mu\text{m/s}$ ; ▲: 1000  $\mu\text{m/s}$ ). The PSA consisted of a solvent-borne poly(2-EHA) containing 10 wt.-% AA.

polymers.<sup>43</sup> Upon neutralization interaction between polymer chains changes from hydrogen bonds to ionic dipolar interactions. Anion formation leads to a characteristic band at  $1575\text{ cm}^{-1}$  representing the carboxylate group. Comparing ATR-IR spectra of neutralized samples shows that DMEA treated samples give also noticeable absorptions for the carboxylate group (Figure 5). Detection of a carboxylate band for DMEA neutralized samples proves incomplete evaporation and is connected to the high boiling point of DMEA ( $T_b$ :  $131\text{ }^\circ\text{C}$ ). It is expected that partial evaporation of DMEA during drying at  $75\text{ }^\circ\text{C}$  further lowers the influence of anion formation on probe-tack in the final PSA. Yet, no complete evaporation of DMEA takes place for all shown samples which is reflected in a detectable carboxylate band at  $1575\text{ cm}^{-1}$  for different degrees of neutralization (0%: 0; 25%: 0.31; 50%: 0.64). However, no difference in probe-tack behavior is detected for differently dried DMEA neutralized samples with and without reduced pressure indicating an only small influence of incomplete evaporation on probe-tack (Figure S3). In addition, no difference in peel and shear is detected for PSA with different degrees of neutralization. Thus, volatile bases like DMEA are suitable for the preparation of secondary dispersions with sufficient tack and are used in further experiments.

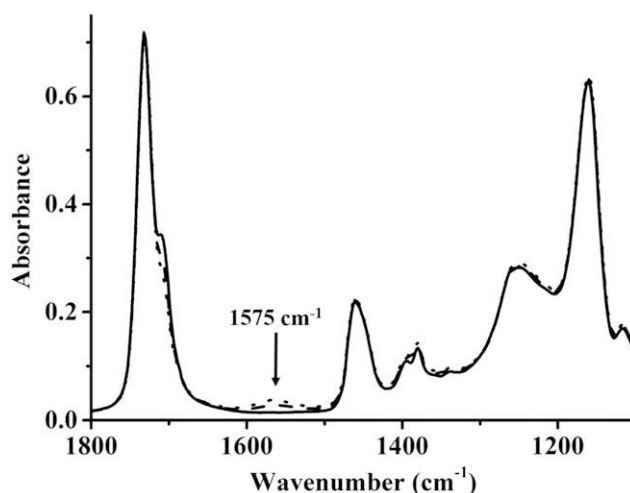
#### Preparation and Stability of Secondary Dispersions

Based on the abovementioned results a solvent-borne copolymer consisting of 10 wt % AA was used for the preparation of a secondary dispersion by consecutive neutralization with DMEA and emulsification in water. These conditions lead to a PSA with an amount of AA high enough for later crosslinking but also sufficient tack prior and after partial neutralization with DMEA. Reproducibility is verified by similar particle size distributions for three identically prepared secondary dispersions (Table S2), with a mean diameter of  $519\text{ nm}$  ( $\pm 32\text{ nm}$ ). This result indicates that secondary dispersions can be prepared with sufficient reproducibility by this method. Although particle size distributions are reproducible the absence of surfactants in

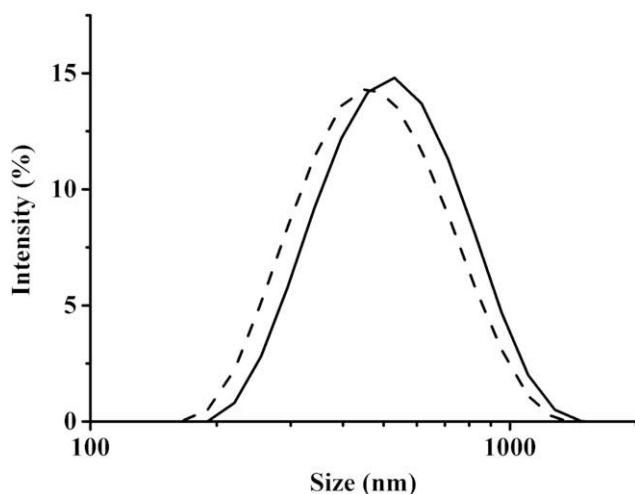
combination with comparably high particle diameters might lead to sedimentation. This does not take place as no sedimentation and change in particle size distribution is observed within 6 months after preparation of the secondary dispersion (Figure S4). In addition, an indication of the stability is given by the tendency of sedimentation as well as change in particle size distribution after centrifugation. Particle size distributions of one centrifugated sample and one noncentrifugated sample gave almost identical particle size distributions (Figure S5). This result correlates well with an only small decrease in solid content from 36 to 32% after centrifugation. The decrease of solid content originates from the sedimentation of particles which was observed as small amounts of residue remaining in the centrifugation tube. Due to the low tendency of sedimentation and constant particle size distributions the secondary dispersions are long term stable. Long term stability could be attributed to sufficiently high amounts of carboxylate groups on the particle surface leading to sufficient repulsive forces giving colloidal stability and thus hindering aggregation and sedimentation of particles. Yet, a time dependent shift (Figure S6) in particle size distribution from  $499\text{ nm}$  ( $\pm 10$ ) to  $443\text{ nm}$  ( $\pm 8\text{ nm}$ ) is observed for the diluted secondary dispersion (DLS samples) over a period of 24 h as presented in Figure 6. Thus, dilution of the reported secondary dispersions leads to the formation of new equilibrium particle size distributions. It is therefore likely that the reported secondary dispersion exhibits changes in particle size distributions upon mixing with other dispersions.

#### Preparation of Reactive PSA with Improved Tack

As mentioned previously, the aim of this work was to obtain reactive PSA with sufficient tack for fixation of parts prior to the final cure. Figure 7 provides the structure of the solvent borne copolymer and the crosslinking of the carboxylic acid groups with epoxy groups at elevated temperatures. In order to prepare reactive PSA the secondary dispersion providing tack and reactive carboxylic acid groups is mixed with an epoxy resin

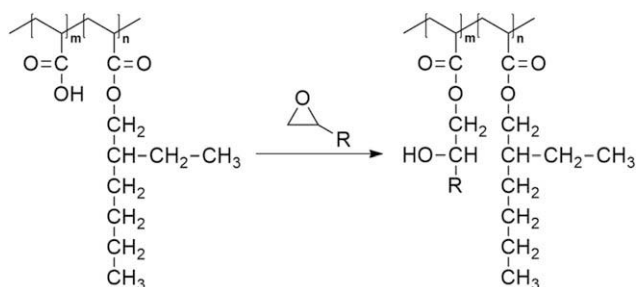


**Figure 5.** ATR-IR spectra of a DMEA neutralized solvent-borne copolymer with different degrees of neutralization (continuous: 0%; dashed: 25%; dotted: 50%). The solvent borne copolymers were cast onto a glass plate with a wet thickness of  $80\text{ }\mu\text{m}$  and dried for 0.5 h at  $75\text{ }^\circ\text{C}$ . The PSA consisted of a solvent borne poly(2-EHA) containing 10 wt % AA.

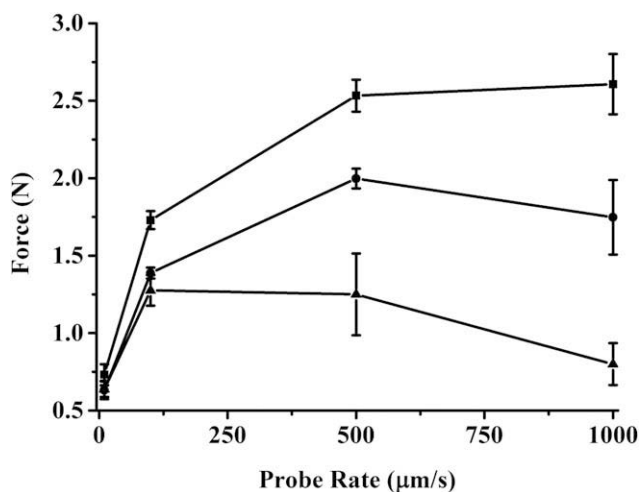


**Figure 6.** Particle size distributions of a secondary acrylic dispersion prepared according to the acetone process with different storage times of the diluted (0.5%) samples (continuous: 0 h; dashed: 24 h). The PSA consisted of a solvent-borne poly(2-EHA) containing 10 wt % AA while the degree of neutralization was 30% with DMEA.

dispersion providing no tack and a number average particle size of about 2  $\mu\text{m}$  which is one order of magnitude larger to that of the secondary dispersion. Different mixing ratio of both dispersions should give a variation in probe-tack of the reactive PSA in advance of curing as illustrated in Figure 8. This Figure shows that the reactive PSA containing 22 and 36 wt % epoxy resin of the total solid content give increasing probe-tack with higher probe rates (cohesive failure at all shown rates). However, high contents of epoxy resin (53 wt % of the total solid content) lead to PSA with inevitable loss of probe-tack, especially at high probe rates (adhesive failure at all shown velocities). As expected, probe-tack decreases with increasing amounts of solid epoxy resin. It should be noted, however, that all shown reactive PSA have considerable amounts of probe-tack which is important for fixation of parts. Of particular interest are reactive PSA within the range 22 and 36 wt % epoxy resin because of cohesive failure over a wide range of probe rates indicating soft polymers with sufficient flow and wetting ability at ambient conditions. The peel force and shear of the reactive PSA in advance of curing are given in Table III and is in accordance with the probe-tack trends from Figure 8. PSA containing 22



**Figure 7.** Structure of the solvent borne random copolyacrylate with 2-EHA and AA as monomers. Addition of epoxy resins to the polyacrylate results in crosslinking at elevated temperatures.



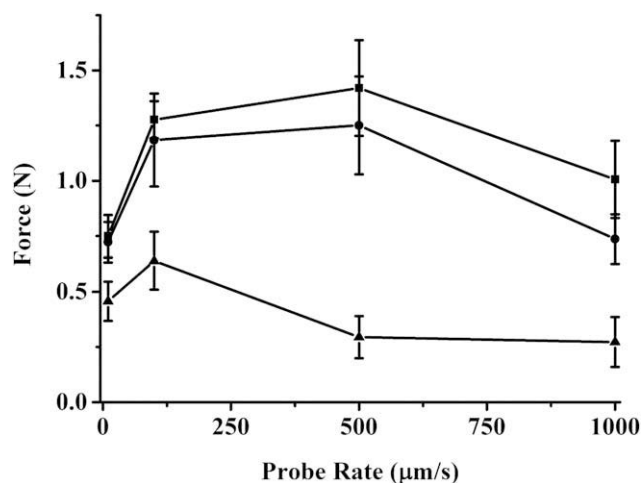
**Figure 8.** Dependence of probe-tack for reactive PSA films cast from a mixture of a secondary dispersion with an epoxy resin dispersion on mixing ratio (■: 22 wt %; ●: 36 wt %; ▲: 53 wt % epoxy resin of the total solid content) and probe rate (10, 100, 500, 1000  $\mu\text{m/s}$ ).

and 36 wt % epoxy resin give PSA with peel values of 0.58 and 0.52 N/mm (cohesive failure) further proving reactive PSA with sufficient flow and wetting ability. On the contrary 53 wt % epoxy resin led to a complete loss of peel. Yet, shear of all shown reactive PSA are very similar indicating no significant amounts of crosslinking taking place. However, after 2 weeks of storage all reactive PSA show significant decrease in probe-tack with adhesive failure at all shown mixing ratio and probe rates (Figure 9) due to crosslinking at room temperature. The presence of tertiary amines such as DMEA are well known for curing of mixtures of acrylic polymers with carboxylic acid groups and epoxy resins under ambient conditions.<sup>39,40</sup> A further study with more focus on the preparation of storage stable PSA by separation of the epoxy phase and DMEA is therefore suggested. Previous research has shown that encapsulation of an epoxy resin by acrylic polymers and polyurethanes give storage stable dispersions after neutralization with triethylenetetramine (TETA).<sup>55</sup> However, these encapsulated systems also exhibit crosslinking after film formation due to rupture of the latex and thus contact of TETA and the epoxy resin. In future investigations, it might be possible to use a different base with high volatility such as ammonia ( $\text{NH}_3$ ) which is expected to be removed during the drying stage and thus increasing the storage stability of final reactive PSA. On the whole, the probe-tack

**Table III.** Peel Force and Shear of Reactive PSA Containing 0, 22, 36, and 53 wt % Epoxy Resin of the Total Solid Content

Epoxy resin content (wt %)	Peel (N/mm)	Mode	Shear (min)	Mode
0	$0.63 \pm 0.05$	CF	$10.5 \pm 0.12$	CF
22	$0.58 \pm 0.01$	CF	$91.7 \pm 15.3$	CF
36	$0.52 \pm 0.04$	CF	$110.6 \pm 22.2$	CF
53	—	AF	$119.2 \pm 2.9$	CF

AF, adhesive failure; CF, cohesive failure.

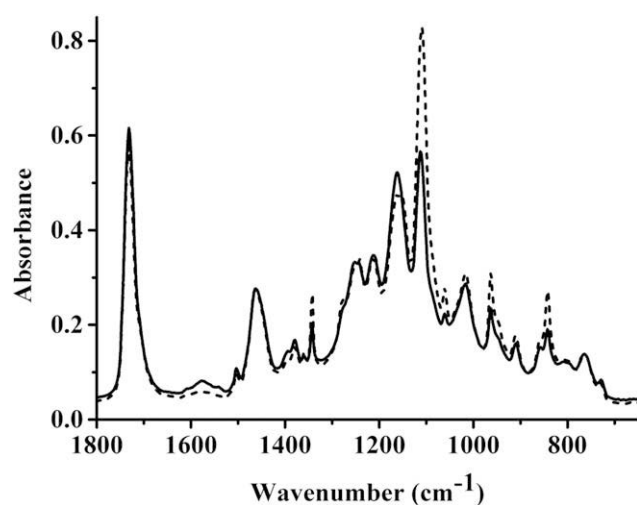


**Figure 9.** Dependence of probe-tack after 2 weeks of storage at ambient conditions for reactive PSA films cast from a mixture of a secondary dispersion with an epoxy resin dispersion on mixing ratio (■: 22; ●: 36; ▲: 53 epoxy resin of the total solid content) and probe rate (10, 100, 500, 1000 μm/s).

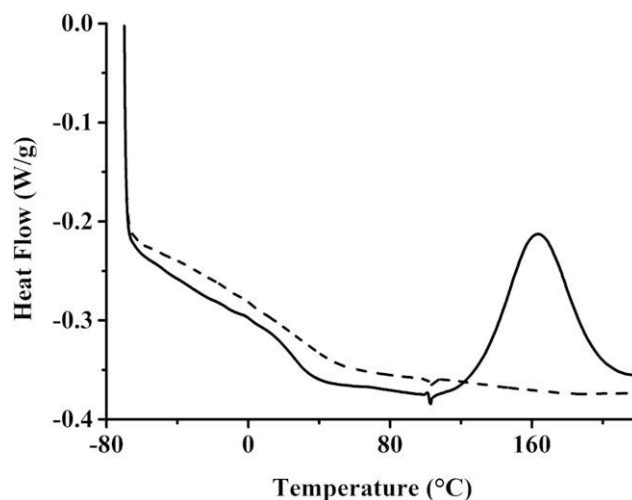
experiment is a straightforward analysis procedure for estimating the rheological behavior and stability of the presented reactive PSA.

#### Post-Crosslinking and Mechanical Properties of Cured Reactive PSA

In general, we observed that sedimentation of the epoxy resin took place for both the epoxy dispersion itself as well as mixtures with the secondary dispersion and during film formation. Therefore, sedimentation within the reactive PSA film might lead to an epoxide gradient over the film thickness. A similar separation behavior is known from literature for an epoxy-acrylic composite latex.<sup>46</sup> Figure 10 illustrates the ATR-IR spectra of one thick polymer film (5000 μm wet thickness, drying time of 24 h at ambient conditions, plus 48 h at 40 °C) showing



**Figure 10.** ATR-IR spectra of both sides of a dried reactive PSA film containing 53 wt % epoxy resin of the total solid content (continuous: facing release liner; dashed: facing air). The PSA film was prepared with a wet thickness of 5000 μm.



**Figure 11.** DSC thermograms of a reactive PSA containing 53 wt % epoxy resin of the total solid content. The same sample was measured in two consecutive runs with 10 K/min (continuous: first run; dashed: second run).

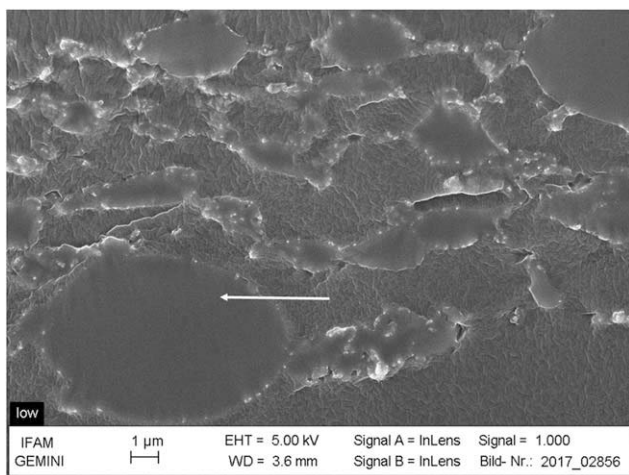
spectra of both polymer film sides (facing air vs. release liner). However, spectra of this thick film (Figure 10) and thick films with lower epoxy resin contents (Figures S7 and S8) show different compositions for both sides due to sedimentation of the epoxy particles. Thus, the thick polymer film gave a side with tack (facing air) and without tack (facing release liner). This behavior further indicates sedimentation due to increased cross-linking density and decreased tack in the lower part of the thick polymer film. High wet thicknesses lead to slow film formation and thus give more time for the sedimentation of the epoxy resin. Reduction of sedimentation was obtained by preparation of thinner polymer films (250 μm wet thickness) with reduced drying times (0.5 h at 75 °C) and thus faster film formation. In general, the thicknesses of post-crosslinked polymer films (60–100 μm) with different epoxy resin contents (22, 36, 53 wt % epoxy resin of the total solid content) were well above the sampling depth of ATR-IR (10 μm). Therefore, ATR-IR was sufficient for examination of sedimentation within thinner polymer films. These post-crosslinked polymer films (1.5 h at 115 °C) showed almost identical ATR-IR spectra of both polymer film sides (facing air vs. release liner) for 22 and 36 wt % epoxy resin of the total solid content (Figures S9 and S10) which is connected to the homogeneous composition owing to the absence of sedimentation during film formation and curing.

**Table IV.** Reaction Enthalpies for Reactive PSA and Lap-Shear Strengths for Post-Crosslinked PSA Containing 22, 36, and 53 wt % Epoxy Resin of the Total Solid Content

Epoxy resin content (wt %)	Reaction enthalpy (J/g)	Lap-shear (MPa)	Mode
22	42	2.5 ± 0.2	CF
36	41	3.9 ± 0.4	CF
53	39	4.3 ± 0.3	CF

CF, cohesive failure.





**Figure 12.** SEM image of a post-crosslinked polymer film containing 22 wt % epoxy resin of the total solid content after cryofracture (residual epoxy phase highlighted by white arrow).

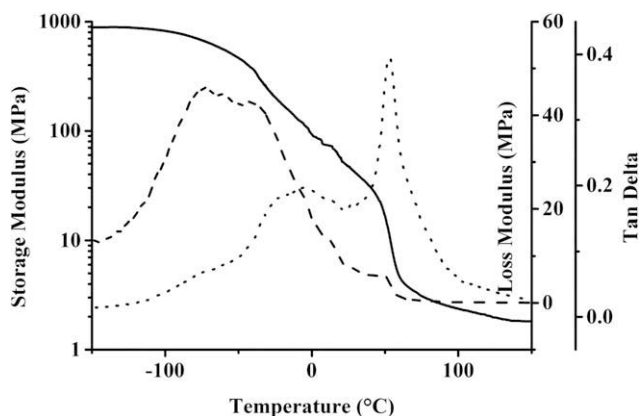
However, ATR-IR spectra of a thin post-crosslinked polymer film with an epoxy resin content of as high as 53 wt % of the total solid content reveal different compositions and thus sedimentation (Figure S11).

To determine reactivity of the reactive PSA DSC measurements were carried out. Figure 11 shows the results for two consecutive runs of the reactive PSA containing 53 wt % epoxy resin. As can be seen, crosslinking took place at about 160 °C. This kind of exothermic reaction did not occur in the second run confirming that all possible reaction takes place in the first run. However, incomplete mixing as well as incomplete crosslinking is indicated by similar reaction enthalpies for all mixing ratio (Table IV). Moreover, all reported reactive polymer films are opaque prior, during and after curing suggesting that both dispersions are not compatible on the molecular level, although no coagulation of the two component dispersions takes place.

SEM of cryofractured surfaces of the cured adhesive provides insight into the heterogeneity of all presented reactive PSA. Figure 12 shows a fractured surface for a crosslinked thin film with 22 wt % epoxy resin (SEM for increased epoxy resin contents in Figures S12 and S13). It is apparent from this figure that both phases did not undergo complete molecular mixing as two phases with different appearances are present. Thus, changes in epoxy resin contents had no influence on molecular mixing

**Table V.** Storage Moduli at Different Temperatures of Post-Crosslinked Polymer Films Containing 22, 36, and 53 wt % Epoxy Resin of the Total Solid Content

Temperature (°C)	Storage modulus, 22 wt % (MPa)	Storage modulus, 36 wt % (MPa)	Storage modulus, 53 wt % (MPa)
-150	893	717	685
0	94	144	267
150	2	2	3



**Figure 13.** DMA of a post-crosslinked polymer film containing 22 wt % epoxy resin of the total solid content (continuous: storage modulus; dashed: loss modulus; dotted: tan  $\delta$ ).

which is in accordance to the similar reaction enthalpies obtained from DCS measurements (Table IV). Adhesion properties regarding lap shear strength and failure mode of the finally post-crosslinked polymer films are presented in Table V. Lap shear strengths slightly increase with the content of epoxy resin. This is mainly because increasing amounts of epoxy resin led to higher degrees of crosslinking and thus higher cohesive strengths. In comparison with typical structural adhesives having lap shear strengths above 5 MPa, all shown post-crosslinked PSA have shear strengths below 5 MPa which is connected to brittle cohesive failure during testing. We expect that the residues unreacted solid epoxy phase within the post-crosslinked samples lead to weakening of the cured adhesive and that they function as crack initialization due to the large size and hardness. Incompatibility of both phases is assumed to be caused by differences on the molecular level of the polyacrylate and epoxidized ortho-cresylic novolac. This result is consistent with previous work in which an epoxy/phenolic/acrylic resin dispersion was prepared according to the acetone process and gave separated phases after curing.<sup>49</sup> The heterogeneity of the films translates into the mechanical properties of the post-crosslinked polymer as illustrated by DMA in Figure 13 (DMA for increased epoxy resin contents in Figures S14 and S15). As evident from tan  $\delta$ , softening of the polymer takes place at 60 °C correlating well with the melting point of the epoxy resin obtained from DSC measurements. This shows that part of the epoxy phase form particles inside the continuous matrix leading to a modulus increase. Table V presents an overview of the storage moduli of all post-crosslinked polymer films at different temperatures. It can be seen from the data in Table V that the storage moduli are high and similar for all samples at -150 and 0 °C while at higher temperatures a complete loss of storage moduli due to melting of the unreacted epoxy phase is observed.

## SUMMARY AND CONCLUSIONS

A reactive PSA was successfully prepared by combination of a secondary dispersion providing tack and a solid epoxy resin dispersion for crosslinking.

- Probe-tack provided insight into the dependence of tack on the content of acrylic acid of solvent-borne copolymers based on AA and EHA. An amount of 10 wt % acrylic acid was found to be sufficient for good tack and final crosslinking. On the other hand, neutralization with different bases led to complete loss of tack (NaOH) or robust tack (DMEA). ATR-IR confirmed anion formation upon neutralization but also incomplete evaporation of DMEA caused by the high boiling point ( $T_b$ , 131 °C) in comparison with the drying conditions (75 °C). The peel, shear, and probe-tack of a PSA (10 wt % AA) were independent on the DMEA content due to low anion formation. Hence, DMEA proves to be a suitable base for self-emulsifying solvent-borne PSA. Preparation of the secondary dispersion was analogous to the acetone process and led to long term stable dispersions.
  - Mixtures of the secondary dispersion with a solid epoxy resin dispersion works as reactive PSA with sufficient peel and shear. In comparison with a non-reactive PSA without epoxy resin the reactive PSA tend to have improved shear but almost the same peel strength. Probe-tack has shown that all reactive PSA are not long term stable under ambient conditions. It would be interesting to compare the storage stability of reactive PSA based on a secondary dispersion which is prepared by neutralization with ammonia instead of DMEA. It is expected that different volatilities of both bases give different amounts of base remaining after the drying stage and thus lead to different storage stabilities. Long drying times and high layer thicknesses lead to inhomogeneities due to sedimentation of the epoxy resin particles. Thus, short drying times are required to exclude sedimentation.
  - All post-crosslinked PSA gave lap-shear strengths close to 5 MPa and could lead to structural adhesives if molecular mixing between the reactive polyacrylate and the solid epoxy resin is further improved. Future work should therefore include optimization of the material properties especially in terms of molecular mixing as well as brittleness and toughening of the final structural adhesive. This will include improvement of molecular mixing prior to crosslinking by substitution of the solid epoxy resin by an epoxy resin based on acrylate monomers for better compatibility with the polyacrylate providing tack.
- Arshady, R. *Colloid Polym. Sci.* **1992**, *270*, 717.
  - Schlarb, B.; Rau, M. G.; Haremza, S. *Prog. Org. Coat.* **1995**, *26*, 207.
  - Schlarb, B.; Haremza, S.; Heckmann, W.; Morrison, B.; Müller-Mall, R.; Rau, M. G. Proceedings of the 21st International Conference in Organic Coatings Science and Technology, **1996**; Vol. 29, p 201.
  - Nanda, A. K.; Wicks, D. A. *Polymer* **2006**, *47*, 1805.
  - Sardon, H.; Irusta, L.; Fernández-Berridi, M. J.; Luna, J.; Lansalot, M.; Bourgeat-Lami, E. *J. Appl. Polym. Sci.* **2011**, *120*, 2054.
  - Saw, L. K.; Brooks, B. W.; Carpenter, K. J.; Keight, D. V. *J. Colloid Interface Sci.* **2003**, *257*, 163.
  - Saw, L. K.; Brooks, B. W.; Carpenter, K. J.; Keight, D. V. *J. Colloid Interface Sci.* **2004**, *279*, 235.
  - Das, S. K.; Kilic, S. (PPG Industries, Inc.). U.S. Pat. 5,342,878 (**1994**).
  - Steinmetz, W. H. (E. I. Du Pont de Nemours and Company). U.S. Pat. 4,302,373 (**1981**).
  - Schrinner, M. C.; Gewiss, H.-D.; Yuva, N.; Melchior, M. (Bayer Intellectual Property GmbH). U.S. Pat. 2014/0316050 A1 (**2014**).
  - Pfeil, A.; Dreischhoff, D.; Godau, C. (Hoechst Aktiengesellschaft). U.S. Pat. 5,908,902 (**1999**).
  - Probst, J.; Melchior, M.; Hovestadt, W.; Sonntag, M.; Köhler, B.; Jansen, B. (Bayer Aktiengesellschaft). U.S. Pat. 6,962,953 B2 (**2005**).
  - Christenson, R. M.; Maska, R.; Dowbenko, R.; Hockswender, T. R. (PPG Industries Inc.). U.S. Pat. 4,289,674 (**1981**).
  - Zhaoying, Z.; Yuhui, H.; Bing, L.; Guangming, C. *Eur. Polym. J.* **2001**, *37*, 1207.
  - Ahmad, N. M.; Heatley, F.; Britton, D.; Lovell, P. A. *Macromol. Symp.* **1999**, *143*, 231.
  - Ahmad, N. M.; Heatley, F.; Lovell, P. A. *Macromolecules* **1998**, *31*, 2822.
  - Heatley, F.; Lovell, P. A.; Yamashita, T. *Macromolecules* **2001**, *34*, 7636.
  - Zosel, A.; Ley, G. *Macromolecules* **1993**, *26*, 2222.
  - Tamai, T.; Pinenq, P.; Winnik, M. A. *Macromolecules* **1999**, *32*, 6102.
  - Qie, L.; Dubé, M. A. *J. Appl. Polym. Sci.* **2012**, *124*, 349.
  - Liu, R.; Winnik, M. A.; Di Stefano, F.; Vanketessan, J. *Macromolecules* **2001**, *34*, 7306.
  - Aradian, A.; Raphaël, E.; Gennes, P.-G. D. *Macromolecules* **2000**, *33*, 9444.
  - Tobing, S. D.; Klein, A. *J. Appl. Polym. Sci.* **2001**, *79*, 2230.
  - Tobing, S. D.; Klein, A. *J. Appl. Polym. Sci.* **2001**, *79*, 2558.
  - Czech, Z. *Eur. Polym. J.* **2004**, *40*, 2221.
  - Lee, S.-W.; Park, J.-W.; Park, C.-H.; Kim, H.-J.; Kim, E.-A.; Woo, H.-S. *Int. J. Adhes. Adhes.* **2013**, *47*, 21.
  - Czech, Z. *Int. J. Adhes. Adhes.* **2007**, *27*, 49.
  - Czech, Z. *Polym. Adv. Technol.* **2004**, *15*, 539.

## REFERENCES

- Lovell, P. A. *Emulsion Polymerization and Emulsion Polymers*; Wiley: Chichester, **1997**.
- Keddie, J. L.; Routh, A. F. *Fundamentals of Latex Film Formation: Processes and Properties*; Springer: Dordrecht, **2010**.
- Petrie, E. M. *Handbook of Adhesives and Sealants*; McGraw-Hill: New York, **2000**.
- Melchior, M.; Sonntag, M.; Kobusch, C.; Jürgens, E. *Prog. Org. Coat.* **2000**, *40*, 99.
- Liu, Y.; Gajewicz, A. M.; Rodin, V.; Soer, W.-J.; Scheerder, J.; Satgurunathan, G.; McDonald, P. J.; Keddie, J. L. *J. Polym. Sci. Part B: Polym. Phys.* **2016**, *54*, 1658.
- Liu, Y.; Soer, W.-J.; Scheerder, J.; Satgurunathan, G.; Keddie, J. L. *ACS Appl. Mater. Interfaces* **2015**, *7*, 12147.

35. Taylor, J. W.; Winnik, M. A. *JCT Res.* **2004**, *1*, 163.
36. Czech, Z. *Polym. Int.* **2003**, *52*, 347.
37. Pedraza, E. P.; Soucek, M. D. *Polymer* **2005**, *46*, 11174.
38. Park, Y.-J.; Kim, J.-H. *Colloids Surf. A* **1999**, *153*, 583.
39. Chu, F.; McKenna, T. F.; Jiang, Y.; Lu, S. *Polymer* **1997**, *38*, 6157.
40. Sun, S.; Sun, P.; Liu, D. *Eur. Polym. J.* **2005**, *41*, 913.
41. Kawahara, H.; Matsufuji, S.; Goto, T.; Okamoto, Y.; Ogura, H.; Kage, H.; Matsuno, Y. *Adv. Powder Technol.* **2001**, *12*, 521.
42. Xu, Z.; Lu, G.; Cheng, S.; Li, J. *J. Appl. Polym. Sci.* **1995**, *56*, 575.
43. Wang, T.; Canetta, E.; Weerakkody, T. G.; Keddie, J. L.; Rivas, U. *ACS Appl. Mater. Interfaces* **2009**, *1*, 631.
44. Park, C.-H.; Lee, S.-W.; Park, J.-W.; Kim, H. *J. React. Funct. Polym.* **2013**, *73*, 641.
45. Hegedus, C. R.; Pepe, F. R.; Dickenson, J. B.; Walker, F. H. *J. Coat. Technol.* **2002**, *74*, 31.
46. Pan, G.; Wu, L.; Zhang, Z.; Li, D. *J. Appl. Polym. Sci.* **2002**, *83*, 1736.
47. Kojima, S.; Watanabe, Y. *Polym. Eng. Sci.* **1993**, *33*, 253.
48. Kojima, S.; Moriga, T. *Polym. Eng. Sci.* **1993**, *33*, 260.
49. Kojima, S.; Moriga, T. *Polym. Eng. Sci.* **1993**, *33*, 265.
50. Chen, L.; Hong, L.; Lin, J.-C.; Meyers, G.; Harris, J.; Radler, M. *J. Colloid Interface Sci.* **2016**, *473*, 182.
51. Liu, L.; Li, J.; Zhang, X.; Jin, K. *RSC Adv.* **2014**, *4*, 47184.
52. Kawahara, H.; Goto, T.; Ohnishi, K.; Ogura, H.; Kage, H.; Matsuno, Y. *J. Appl. Polym. Sci.* **2001**, *81*, 128.
53. Lindner, A.; Lestriez, B.; Mariot, S.; Creton, C.; Maevs, T.; Lüthmann, B.; Brummer, R. *J. Adhes.* **2006**, *82*, 267.
54. Lakrout, H.; Creton, C.; Ahn, D.; Shull, K. R. *Macromolecules* **2001**, *34*, 7448.
55. Shi, Y.; Wu, Y.; Zhu, Z. *J. Appl. Polym. Sci.* **2003**, *88*, 470.