

High Performance, Low VOC Water-Based Pressure Sensitive Adhesives for Automotive Applications

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Motivation

With increasing environmental and health awareness and general focus on sustainability topics, the focus of car buyers and automotive manufacturers moves to low odor and low emission of volatile organic compounds (VOCs) inside cars. Additionally, local regulations on car interior air quality have been released in several countries and more or tighter regulations are currently in discussion.

From this, a strong driving force for water-based PSA products with low VOC content and low odor threshold has evolved. At the same time, a high adhesive performance and resistance to harsh temperature and chemical conditions is needed. Furthermore a variety of materials build in car interior, which leads to demanding requirements for adhesion to various polar as well as low surface energy (LSE) surfaces.

Furthermore, the odor of a car's interior is gaining more and more public awareness. For certain regions in the past, the typical "new car" smell was a sign of quality, whereas in other regions, odor is not preferred by the customers and threshold targets are set strictly low. Also for odor testing, national association guidelines (e.g. VDA 270) or automotive OEM standards are defined.

Performance Requirements of PSAs for Automotive Tape Applications

When developing a new PSA for automotive applications, VOC level and odor must be taken into account in addition to the typical criteria like matching peel & shear profile, high performance at elevated temperature, or resistance to moisture, chemicals, plasticizer and aging.

Solvent borne acrylic PSAs are widely used for manufacturing of specialty tapes due to their excellent performance, achieving high peel – high shear performance profiles covering different substrates and carriers. In the past, water-borne acrylic PSAs were falling short, struggling to achieve both, high peel and high shear combined with good heat performance and resistance to surrounding conditions.

With recent developments, new water-borne acrylic products were developed matching the high performance standard needed. We benchmarked three unformulated high performance products (HPP1, HPP2 and HPP3) at 50 g/m² dry coat weight against a commercially available UV-syrup acrylic PSA technology (final designed tape, dry coat weight unclear) (see Figure 1). The HPP

products maintain a comparable level of peel to either of the two benchmarks. Especially on polar surfaces the adhesion performance is very convincing. For PVC as a critical substrate due to a certain load of plasticizers we found a convincing performance for all three products, which is comparable to the peel properties on stainless steel. This indicates a good plasticizer resistance of the three grades. Also on LSE substrates, HDPE, HPP1 and HPP3 can deliver a convincing level of adhesion comparable to Benchmark 1. HPP2 displays a lower adhesion on HDPE, but still outperforms Benchmark 2. From this analysis we conclude that a competitive peel performance compared to market leading benchmarks can be achieved when formulating a PSA for specialty tape applications on demanding surfaces.

180° Peel Adhesion after 24 Hours Dwell Time

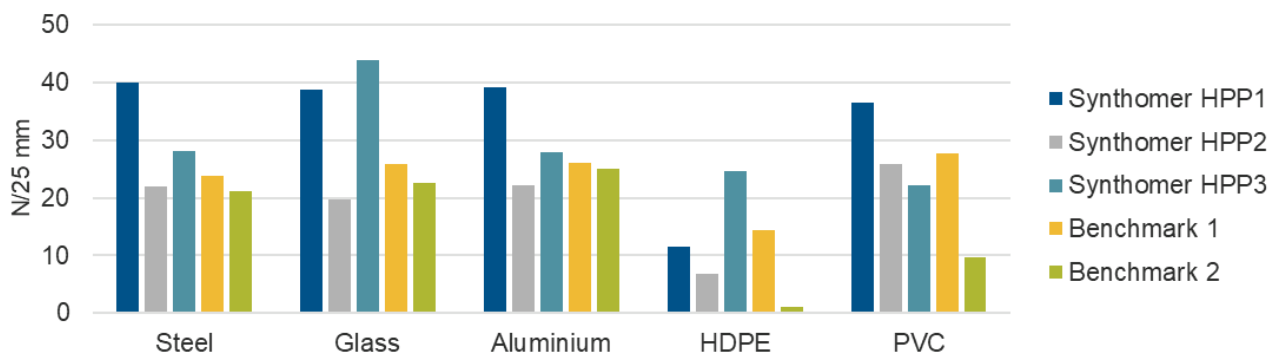


Figure 1: 180° peel adhesion after 24 hours dwell time on different substrates.

We also looked at the performance at heat/elevated temperature, which is important when thinking of applications close to car engine or heated car interior in the summertime (see Figure 2). Here we found competitive shear properties and shear adhesion failure temperatures (SAFT) for HPP1 and HPP2 compared to the benchmark products. HPP2 is a tackified grade specifically designed for LSE applications and therefore lacks shear at very high temperature, but still shows excellent shear performance at 23 °C comparable to HPP1, HPP3 and the two benchmarks.

High Temperature Performance

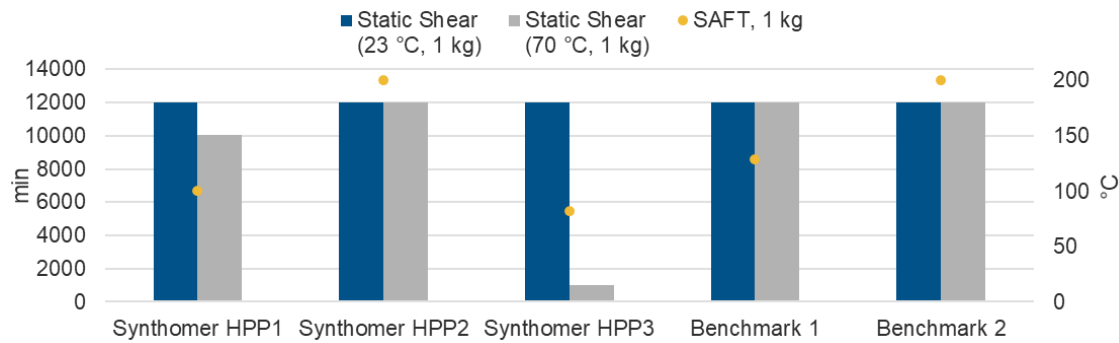


Figure 2: Static shear at different temperatures (in minutes) and shear adhesion failure temperature (in °C).

Volatile Organic Compounds (VOCs)

The world health organization (WHO) and the United States Environmental Protection Agency (EPA) distinguish volatile organic compounds by their boiling points, dividing the whole majority of vaporizable substances into different classes:

Table 1. Classification of volatile organic compounds.[1,2]

Type	Abbreviation	Boiling Point Range / °C	Examples (boiling point)
Very volatile organic compounds	VVOC	<0 to 50 – 100	Acetone (56 °C) Ammonia (-33 °C) Formaldehyde (-19°C)
volatile organic compounds	VOC	50 – 100 to 240 – 260	Ethylene glycol (197 °C) Ethanol (78 °C) Canola methyl ester (345 °C)
Semi-volatile organic compounds	SVOC	240 – 260 to 380 - 400	Squalene (275 °C) DINP (267 °C) Dibutyl phthalate (340 °C)

There are many standards for VOC analysis from industry associations or automotive OEMs. Typically, it is differentiated between VOC (up to C25) and FOG (C14 to C32) analysis [3]. Numerous test standards are available depending on national association guidelines (e.g. VDA 278 [3]) or automotive OEM standards. This can include various test setups like thermodesorption or headspace, bag or chamber testing and can be limited to certain substance classes like formaldehyde and aldehydes (VDA 275 [4]) or include all emitted substances in a certain temperature window. Contracted analysis in certified laboratories is easy to realize.

The regional markets have a different focus and requirements for low VOC automotive products. In particular, the Asian market is leading a more restrictive policy against VOC emissions with defined national targets for overall VOC and limitations for amounts of defined critical

substances (e.g., JAMA, GB/T 27630-2011)[5,6]. The typical “new car smell” is not preferred. The European market is characterized by standardized test methods based on national car association input (e.g., VDA). The limitations are less strict than in the Asian market. In the American region the awareness for VOCs and impact on health and environment has also increased and consumers are much more conscious of car interior smell and clean air quality. Additionally, there are quality specifications by each automotive OEM, which can be even stricter than national regulations.

As shown in Figure 3, the VOC and FOG level can vary quite drastically if comparing low VOC samples with non-optimized products. In the graph, the difference between the low VOC products and the non-optimized sample becomes quite evident. While the optimized products all maintain VOC levels below 100 ppm and FOG levels below 500 ppm, the non-optimized sample exhibits approx. the 10-fold load of VOC and FOG according to VDA 278 analysis.

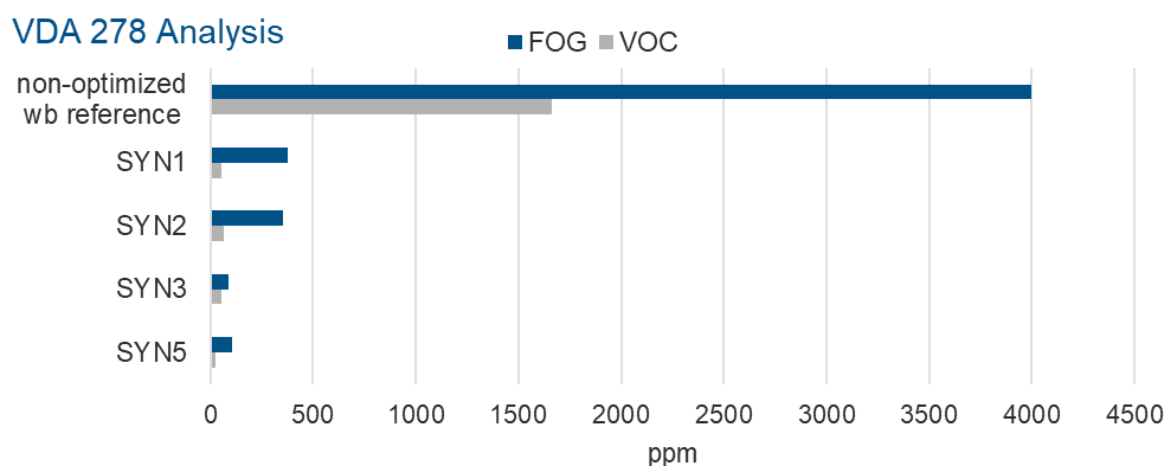


Figure 3: Results for VOC and FOG level of different waterborne acrylic PSAs according to VDA 278 analysis.

Furthermore, a closer look on the most critical substances listed in some national standards (compare Table 1) can also reveal the risk potential of PSA products. In Figure 4, the acrylic water-borne PSA products SYN1, SYN2, SYN3 and SYN4 are compared to the same non-optimized waterborne reference (also an acrylic PSA). It becomes evident that the non-optimized sample has high loads of the critical aldehydes acetaldehyde and formaldehyde, which would prohibit the use of this product under GB/T 27630-2011 although the limits for the other critical substances are met. The low VOC SYN products all pass the GB/T 27630-2011 standard.

Critical VOC Substances

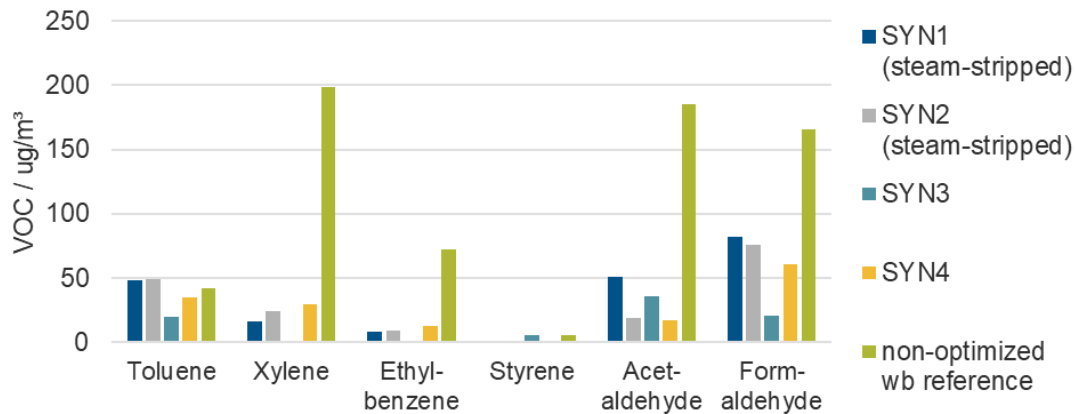


Figure 4: Amount of critical VOCs detected in different waterborne acrylic PSAs.

Related to VOC is also the topic of odor, especially in the closed car interior. Many low volatiles come with a characteristic smell, which can be perceived differently, from comforting (*e.g.*, vanilla scent) to distractive or unpleasant (*e.g.*, ammonia). In general, a low odor inside the car is desired. The odor threshold is affected by the surrounding conditions of moisture and temperature. With increasing temperature and/or humidity, the odor level is likely to increase. To determine the odor level inside a car, VDA 270 [7] has defined testing and evaluation standards. As shown in Figure 5, four low VOC samples from our portfolio (SYN1, SYN2, SYN3, SYN4) were analyzed according to VDA 270 in comparison to the non-optimized waterborne PSA sample.

VDA 270 Analysis

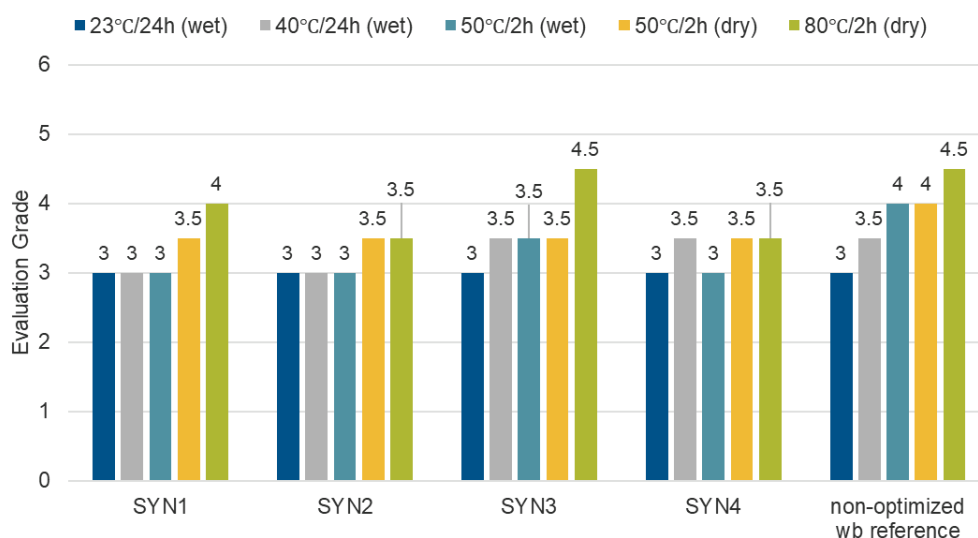


Figure 5: Odor level rating for several waterborne acrylic PSAs after different storage conditions according to VDA 270 analysis.

This graph shows that the overall odor is not linearly related to the VOC or FOG level of a PSA product. The samples have the same rating for odor at 23°C. With increasing temperature and moisture conditions, the odor of the samples changes quite a bit. At the highest temperature, all samples exhibit their highest odor level, with SYN4 having the lowest odor increase.

The Path to Lower VOCs

For solvent-borne pressure sensitive adhesives (PSAs), the solvents used in the manufacture can represent a high load of VOCs in the final tape product. In particular, if the specialty tapes are employed in the car interior, e.g. for mounting of components, fixation of interior parts (ceilings etc.), electrical insulation of cables or organization of cable harnesses, these strictly defined limits can pose a large hurdle to overcome.

Here, water-borne PSAs exhibit the benefit of the non-hazardous basic solvent water. But although the basic of a dispersion adhesive is not of concern, the raw materials used during emulsion polymerization can deliver a large contribution to the overall VOC and odor threshold of the final PSA.

Therein, residual monomers as non-fully transformed reaction residues are one aspect which comes to mind. The level of residual monomers can be moderated by effective redox reaction conditions during polymerization or introduction of a follow-up post-activation redox reaction to convert the remaining monomers into non-volatile compounds. Often residual monomers are mistaken as being synonymous for VOCs, but this is in fact not the case. Also other ingredients of a reaction mixture can increase the VOC load of a product, whether it is ammonia for pH adjustment or low volatiles coming as impurities in the main raw materials or formulation additives. Some chemicals can even create VOCs during reaction because they are sensitive to the reaction conditions (pH, redox potential). Therefore, deliberate selection of raw material type and quality are crucial for successful development of PSA products which fulfill the strict VOC and odor requirements of automotive OEMs.

If a product with excellent performance for the target application was identified, but VOC and odor are out of range for application in the automotive interior, there are some tactics to improve the existing product. One way would be the modification of the synthesis procedure, e.g. change of monomer feeds or temperature profiles or the aforementioned addition of a chemical post-activation. This can drastically decrease VOC level. Furthermore, exchange of hazardous chemicals can lead to better overall hazard classification of the PSA product. On the downside, the alternative raw materials can be more expensive and have a significant impact on wet and dry product properties, which makes comprehensive recipe adjustment necessary to achieve original properties again (see Case Study 1).

A second option is to introduce a step of physical removal of volatiles by purging the dispersion after polymerization with hot water steam (so called steam-stripping). This physical way of VOC removal is very common for styrene-butadiene rubber products, but is also applicable to acrylic PSAs. The product is exposed to hot water vapor (steam) for several hours and a consecutive reduction of VOCs occurs over time, while the volatiles are taken out of the product together with

the hot steam, which is then condensed and needs to be disposed of. By steam stripping, an efficient reduction of VOCs is possible down to extremely low VOC levels. To be able to apply this harsh technique to a product, the PSA must have an excellent stability to withstand this process without changes. No pH drifting allowed or agglomeration during the stripping process would be critical criteria. In addition to the hazardous condensation waste and harsh reaction conditions, the process has also the disadvantage of being energy and time-consuming process.

The third way to decrease the VOC and odor level of an existing product is to modify the formulation by using higher quality raw materials with lower amount of impurities, the dedicated or the choice of low-VOC formulating agents like defoamers, tackifiers, wetting agents and others. Formulation additives improve the PSA performance, but can also heavily impact the overall VOC load. The benefit of choosing higher purity versions of the same chemicals is an easy replacement without significant influence on the polymer structure. On the other hand, higher purity comes with increased pricing, which raises production costs of the product.

No matter which choice of strategy has been made or even the decision to combine several approaches, the focus should lie on matching the original PSA performance. All described options can impact the PSA on a polymer level or influence the dispersion's coating behavior. The overall goal would be to not change PSA properties due to VOC reduction.

Case Studies

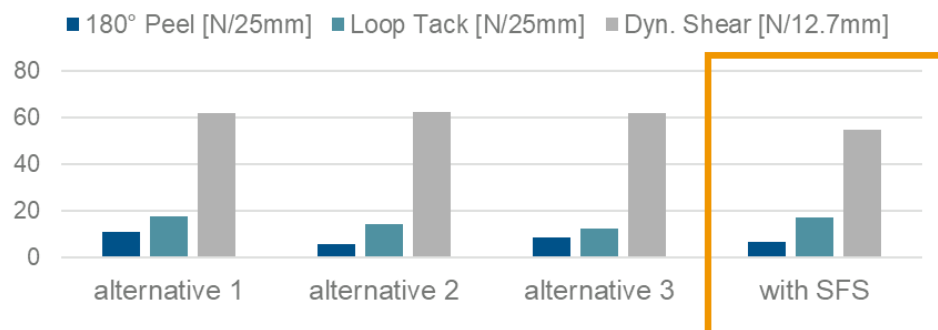
In the past, we have gained deep expertise in development of high performance water-based PSA products with a large variety of performance specifics to satisfy the complexity of requirements set in automotive tape applications.

In the following, several real life examples will demonstrate the typical tripping hazards of PSA developers when it comes to VOC and odor optimization.

Case Study 1 - Modification of Synthesis Procedure

As already mentioned, depending on reactivity or degree of purity, raw materials can contribute to overall VOC level. The exchange of VOC-releasing chemicals for non-releasing alternatives can be challenging. A thorough raw material screening is needed as well as comprehensive tests to check the PSA properties with new raw material. In Figure 6 we see a water-borne PSA product, originally containing the formaldehyde-releasing redox agent sodium formaldehyde sulfoxylate (SFS) (see orange box). Due to increasing regulatory concerns around formaldehyde and its carcinogenic potential, it was decided to replace SFS in this product. Several alternative redox systems were potential candidates (alternative 1 to 3), and the adhesive performance was found to be similar for all three candidates. But not all gave a convincing results when comparing the coating behavior of the original, SFS-containing product with the exchanged systems.

Adhesive Properties



Coating Behavior

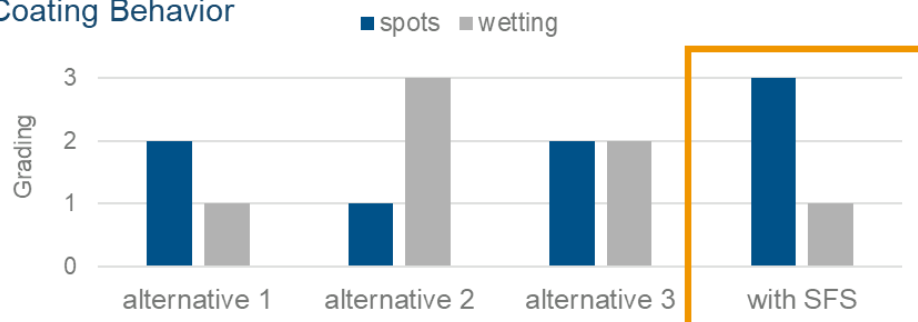


Figure 6: Adhesive properties and coating behavior of SFS-containing PSA compared to formaldehyde-free post-activations for the same PSA product.

Only one system (alternative 1) gave similar results for wetting of the PSA dispersion and even an improvement in spot formation. Therefore, the redox system “alternative 1” was chosen to replace SFS in the PSA recipe.

Case Study 2 – VOC Improvement by Physical Stripping

Let’s look at another example for VOC improvement of a water-based dispersion PSA. Here an acrylic PSA product was improved in total VOC content by “steam stripping” of volatile components. The adhesive properties were maintained as shown in Figure 7.

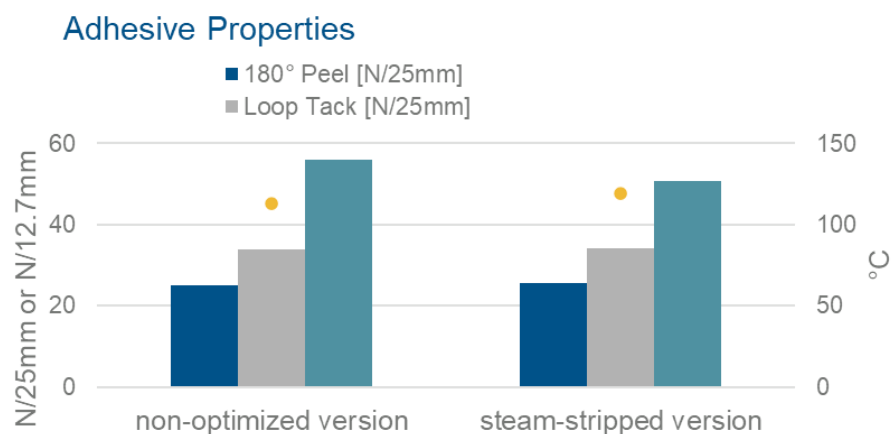


Figure 7: Comparison of adhesive properties of a “regular” emulsion PSA and its steam-stripped version.

Using dynamic mechanical analysis, we made sure that on the polymer scale, no significant changes occurred due to the harsh reaction conditions of steam stripping process. As can be seen in Figure 8, the rheology profile of the dried PSA film is identical for the original product and the VOC-optimized, steam-stripped version.

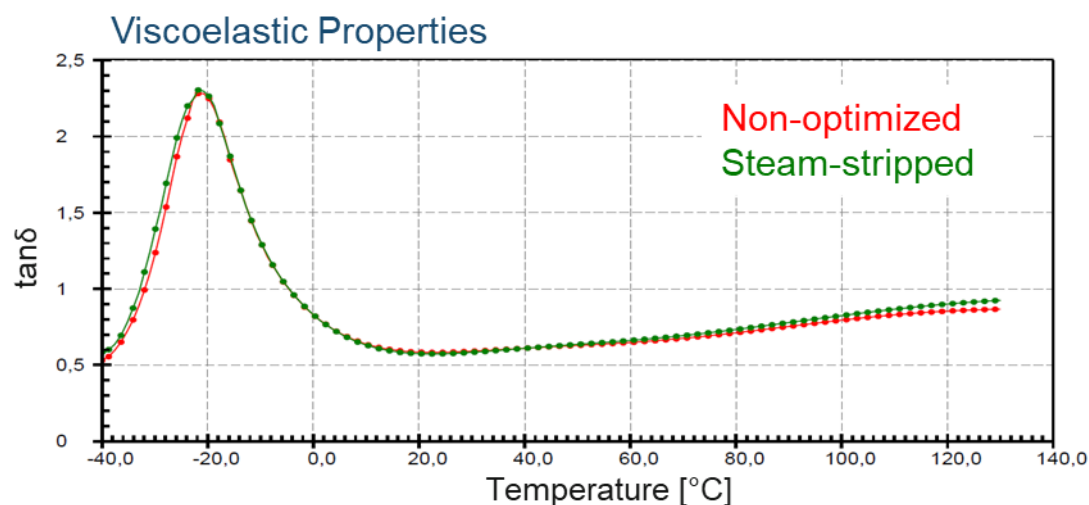


Figure 8: Temperature sweep DMA of a “regular” emulsion PSA and its steam-stripped version.

Case Study 3 - Impact of Formulation Additives

When improving the PSA performance by using additives, such as wetting agents, defoamers or tackifiers, it is possible to involuntarily add VOC to the final product if the additive quality is not carefully selected. The two following real-life examples (Case Study 3 and 4) demonstrate this very well.

Impact of Additives

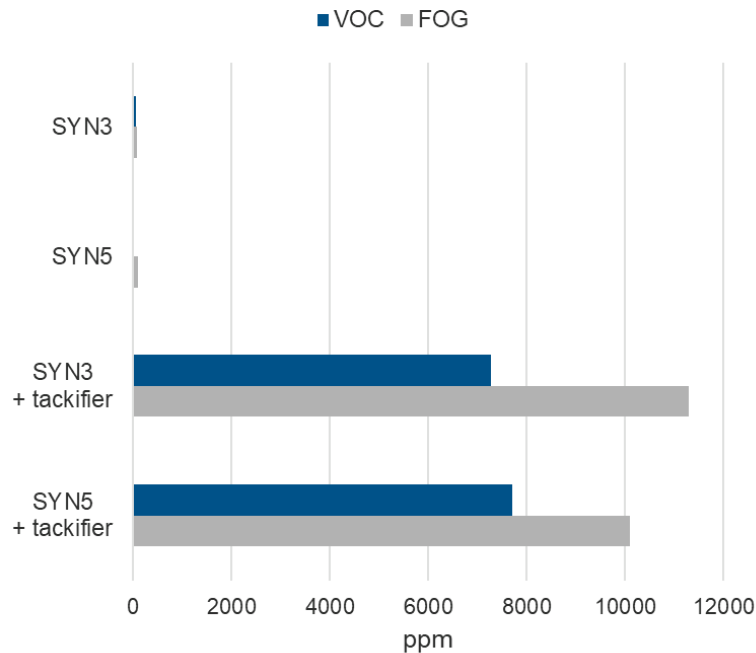


Figure 9: VOC and FOG level of unformulated products SYN 3 and SYN 5 compared to their tackified versions.

In the first example (Figure 9), two low VOC products from our acrylic PSA range (SYN 3 & SYN 5) were chosen for the development of a new specialty tape for automotive interior. The VOC and FOG levels of both products alone at 50 g/m² dry coat weight are below well below 120 ppm.

When formulating the PSAs with a high performance tackifier to increase peel and tack, the overall PSA performance was improved at the cost of high VOC and FOG introduction. The load for both had increased by 100-fold, which marks a drastic rise in VOC and FOG to a level that is not acceptable for automotive interior applications.

Case Study 4 - Low FOG Product Development

In the next case, the impact of defoamer type was found to be a critical parameter in the overall PSA design. A steam-stripped low VOC grade was chosen for a specialty tape development, but during analysis it became clear that despite the low VOC level, the FOG level was too high to be considered for automotive applications (see Figure 10). When trying to reproduce the issue in the lab, we found that the purely synthesized polymer before stripping did not show increased FOG values, whereas the standard production quality had a much higher amount of FOG to which paraffinic substances contributed the most drastically.

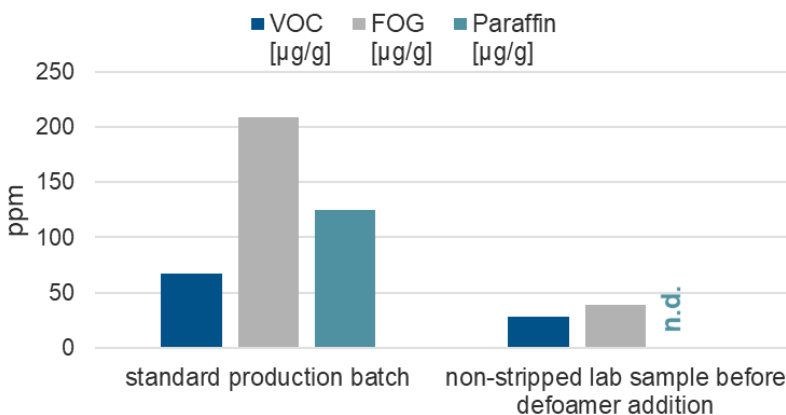


Figure 10: VOC and FOG level of a steam-stripped waterborne acrylic PSA from full scale production vs. a non-stripped lab version of the same polymer.

The level of paraffinic FOG substances helped to narrow down the issue to the defoamer package, where a mineral oil-based defoamer including a paraffinic fraction was used in the original design. By exchanging this with a countertype without a paraffinic fraction, the overall FOG load was drastically improved to a level that allowed the use of the product for automotive interior applications (see Figure 11).

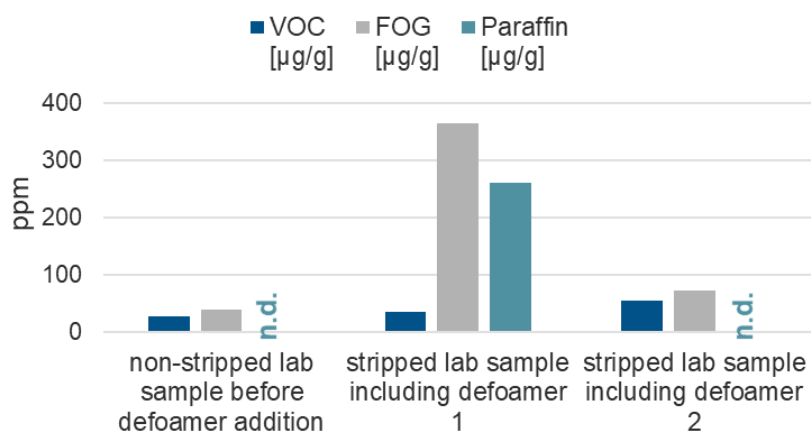


Figure 11: VOC and FOG level of a steam-stripped waterborne acrylic PSA with different defoamer types.

As any change in formulation can have an impact on PSA performance and wetting as shown in Case Study 1, the application properties of the old and new formulation were analyzed at two different coat weights (20 g/m² and 65 g/m²). This analysis confirmed that the overall PSA performance was not negatively impacted by elimination of FOG-increasing paraffinic substances from the formulation (see Figure 12). Furthermore, the wetting of the dispersion remained on an excellent level (see Figure 13), which indicates successful FOG improvement of the acrylic PSA without compromising the outstanding performance.

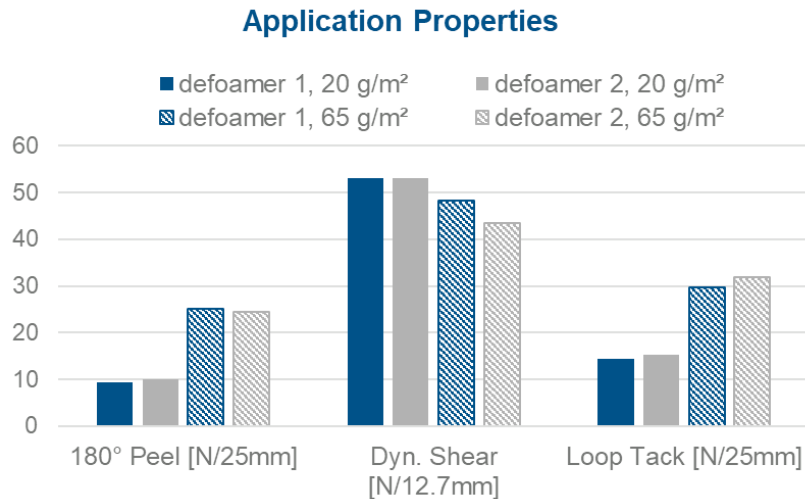


Figure 12: Application properties of a steam-stripped waterborne acrylic PSA with old and new defoamer system.



Figure 13: Wetting properties of a steam-stripped waterborne acrylic PSA with old and new defoamer system.

Conclusion

As discussed in the beginning, specialty tapes need to show excellent adhesion-cohesion balance on variety of substrates, resistance to harsh conditions e.g., high temperature and humidity, as well as maintaining their performance after contact with chemicals (salt water, motor oil, etc.) to be considered for specialty tape applications. To be applied in automotive interiors, the VOC and FOG levels also need to match national and OEM requirements additional to odor threshold. Here, the developer needs to pay attention to the definitions, not falling for the common fallacy of total VOCs being identical with the residual monomer level in a product. Instead, VOCs include residual monomers and furthermore many other volatiles from reaction aids and post-synthesis formulation additives.

Reducing the total VOC and FOG level in an existing product to make it suitable for car interior applications can be energy, time and cost intensive. The modification of existing products to low VOC versions is only possible with circumspect development and careful pre-selection of raw materials. Even small amounts of additives or reaction aids can have a drastic impact on the overall VOC and odor level of a product. Of course, the original PSA target performance always needs to be in considered.

We offers expertise in development of high-performance water-borne PSAs for the demanding requirements of the automotive industry. From the display of several case studies, this expertise was demonstrated. With extensive experience in development and optimization of waterborne PSAs – not only performance-wise, but also in terms of VOC and FOG reduction, the creation of tailor-made solutions for PSA specialty tape applications becomes possible.

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6. Acknowledgments

The authors would like to acknowledge the Marl & Roebuck application lab teams and Marketing & Technical Service Adhesives for their contributions to this work.