



EXPANDING THE PSA FORMULATOR'S TOOLBOX WITH NEW HYDROPHOBIC VINYL ESTER MONOMERS

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Expanding the PSA Formulator's toolbox with new hydrophobic Vinyl Ester monomers

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Introduction

Over the years, waterborne (WB) Acrylic Pressure Sensitive Adhesives (PSAs) have developed a strong position in many label and industrial tape segments, thanks to the many advantages they offer over other technologies¹. Further improvements of their adhesion/cohesion balance, adhesion to low surface energy surfaces and water resistance properties could allow for further growth of these technologies in some specialty label areas (beverage, hard and flexible plastic packages, personal and home care, pharmaceutical and health care, ...) and specialty tapes applications (mounting tapes for transportation and construction,...).

Recently, modification of the acrylic polymer backbone with a flexible and highly hydrophobic vinyl ester derivative containing bulky alkyl groups (Figure 1) has proven to enhance both the adhesion/cohesion balance as well as the water resistance of the final WB PSA product².

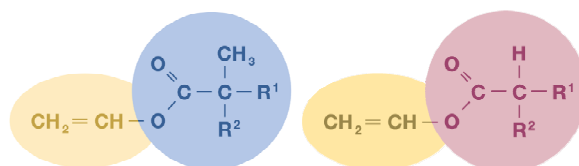


Figure 1: Chemical structure of VeoVa™ 10 monomer (left, R¹ and R² = alkyl groups with a total of 7 Carbon atoms Tg ~ -3 °C), VeoVa™ EH monomer (right, R¹ and R² = alkyl groups with a total of 6 Carbon atoms Tg ~ -36 °C).

The first part of this paper deals with vinyl ester-modified WB Acrylic PSA, where a fundamental investigation of the large strain mechanical properties and adhesive properties of the PSA have been performed in order gain a better understanding on the effect of the highly hydrophobic vinyl ester on the adhesion/cohesion balance of the PSA material.

On the basis of our previous research work on model systems showing the benefits of the hydrophobic vinyl ester, it has been possible to develop prototypes of hydrophobically-modified

acrylic WB PSA showing, even in the presence of a tackifier, excellent adhesion/cohesion balance combined with outstanding water whitening resistance.

The second part of the paper will discuss the most recent advances made on Vinyl Ester PSA, where the polymer backbone of the WB PSA is chiefly composed of soft and hydrophobic (bio-based) vinyl ester monomers. This new concept has enabled us to prepare new polymers showing PSA performances close to that of a solvent-borne (SB) Acrylic PSA. This approach has also led us to design non-polar PSA yielding remarkable adhesion to Low Surface Energy substrates.

Experimental

PSA film preparation:

The latex is adjusted to pH ~7 and applied with a bar coater on a 1 mil polyester film. The gap of the bar coater is adjusted so that the dried PSA film has a thickness of 23 +/-2 or 50 +/-2 μm . The film is dried for one hour at room temperature followed by 3 minutes in the oven at 110 °C. The film is then laminated on a release liner (Siliconized paper) and kept at least for 24 hours under 50% RH and 23 °C before testing.

Tack experiments:

Adhesive films with a thickness around 100 μm were casted on transparent microscope glass slides. Standard values for the approach velocity are used ($V_{\text{app}} = 30 \mu\text{m/s}$), contact time ($t_c = 10$ s), contact force ($F_c = 70$ N) for the probe ($d = 10$ mm), contact surface stainless steel whose contact surface was polished to a mirror finish. The debonding velocity (V_{deb}) was 1000 $\mu\text{m/s}$. All tests were carried out at 23 °C.

Tensile experiments:

PSA samples with a thickness of around 600 μm (e_0) were prepared. The tensile tests were performed on rectangular samples which are 5 mm wide (w_0) and 25 mm length (l_0). A standard tensile tester (Instron 5565) equipped with a video extensometer is used to measure the local strain. The machine uses a 10 N load cell. Initial strain rate was chosen 0.1 s^{-1} . For each set of parameters (sample and velocity), four tests were performed at 23 °C. The data give the nominal stress σ_N as a function of the strain ϵ .

PSA Properties

Adhesion – 180 ° Peel (20' – 24h, SS, Glass, HDPE, LDPE, PP, Teflon, PVF) – according to Finat Testing Method (FTM-1), Tack – Loop Tack Test (1 x 1 inch, SS) – according to FTM-9, Cohesion – Static Shear (1 x 0.5 inch – 1kg, SS) – according to FTM-8.

Water Whitening Test:

To assess the whitening, a piece of PSA film (5cm x 12cm) is immersed in 500 ml of demi water. After 24 hours, the film is removed from the water and applied directly on both black and white parts of the Leneta opacity chart. The opacity is measured immediately (*Ultrascan XE* from *HunterLab*) and compared to that of the non-exposed to water PSA film to obtain the delta opacity value. Each measurement is replicated 3 times. A lower Delta Opacity value means a higher resistance to water whitening.

Results and Discussion

Enhanced adhesion/cohesion balance

The following study aims at further understanding the effect played by the hydrophobic vinyl ester monomer on the overall performance of the final PSA material. In order to evaluate the effect of the hydrophobic monomer, two latexes with a targeted T_g of -30°C were prepared; an all-acrylic and its counterpart containing 20 wt% of VeoVa™ 10. For the sake of comparison, the two systems were prepared under the same polymerization conditions keeping the surfactants, functional monomers types and levels constant. From Figure 2, it is clear that the hydrophobic vinyl ester significantly increases the cohesive strength of the PSA while maintaining a similar level of peel and tack. As discussed elsewhere³, the increased cohesive strength of the vinyl ester modified PSA was likely due to a higher percentage of gel content in the polymer.

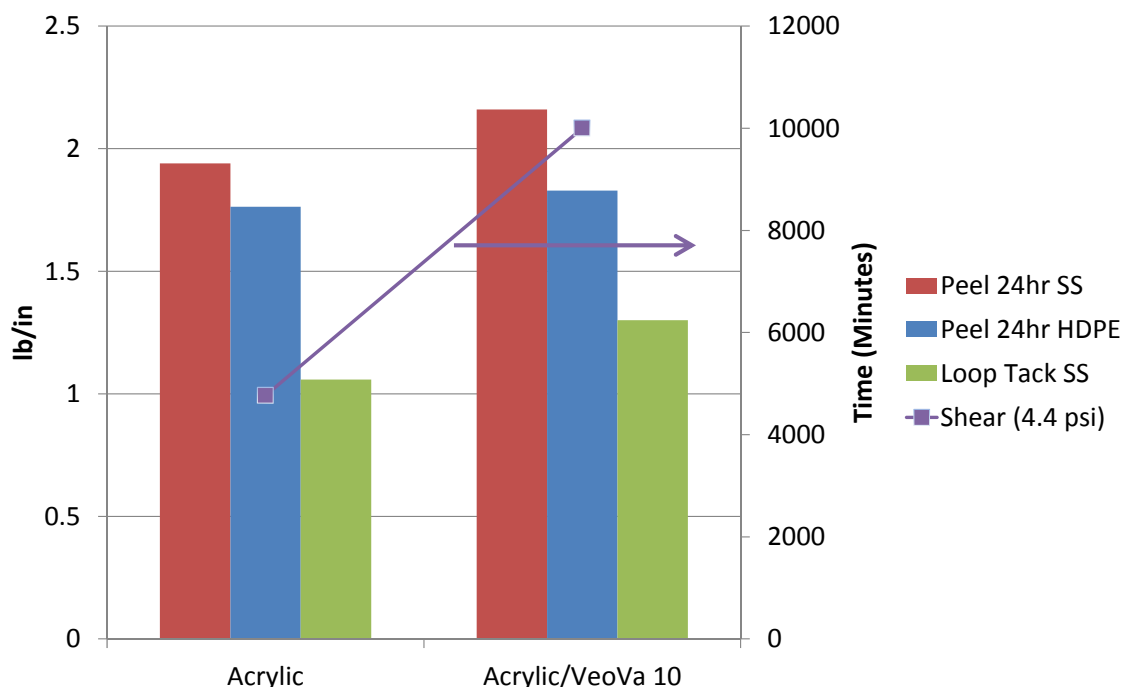


Figure 2: Peel and Shear Performances of WB Acrylic and WB Acrylic/VeoVa PSA.

Although the peel test is an easy way to measure the adhesive strength of a PSA, the probe-tack test provides a stress-strain curve and the shape of this curve allows for the characterization of the de-bonding mechanism of a PSA⁴. During the tests, a probe comes into contact with the adhesive layer and, after a pre-set contact (time and pressure), the probe is de-bonded at a set velocity. Typically, high maximal strain and high-energy adhesion can be reached if the elongation of fibrils is accompanied by energy dissipation. The adhesive properties of the two PSA have been studied in more details through these tack experiments (Figure 3).

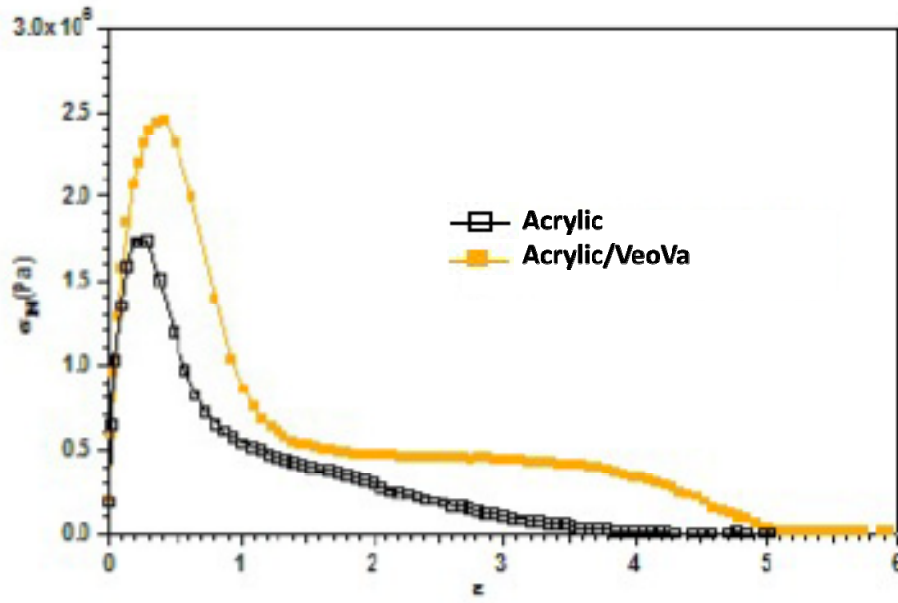


Figure 3: Tack curves using a Stainless Steel Probe.

The adhesion energies are obtained from the area under the curves. At high velocity of debonding (1000 $\mu\text{m/s}$), the adhesion energy for the vinyl ester modified PSA is significantly greater than that of the corresponding All-Acrylic PSA.

Next, it is also of interest to evaluate PSA performance at high strain by tensile experiment⁵. In a standard tensile experiment, the sample is stretched at a constant speed and the force is recorded as function of the displacement. The large-strain behavior can be more easily analyzed by using the reduced stress (σ_R , also named Mooney stress) and strain ($\lambda = l / l_0$). Two important parameters can be obtained from the Mooney stress of a PSA at a particular strain rate: the constant C_{soft} characterizes the stress relaxation of the material at intermediate strains (temporary cross-links). It is defined as the slope of a line fitting the curve between $[1/\lambda_{\text{hard}}, \sigma_R(\lambda_{\text{hard}})]$ and $[0.8, \sigma_R(0.8)]$. After this softening phase, the curve σ_R vs $1/\lambda$ goes through a minimum $[1/\lambda_{\text{hard}}, C_{\text{hard}}]$, which is characteristic of a hardening. C_{hard} has the physical meaning of a modulus considering the permanent cross-links and λ_{hard} is directly related to the chains finite extensibility and thus to the network architecture. The $C_{\text{soft}}/C_{\text{hard}}$ ratio is correlated with the dissipative property of the PSA. The curve of the reduced stress σ_R as a function of $1/\lambda$ is presented in Figure 4.

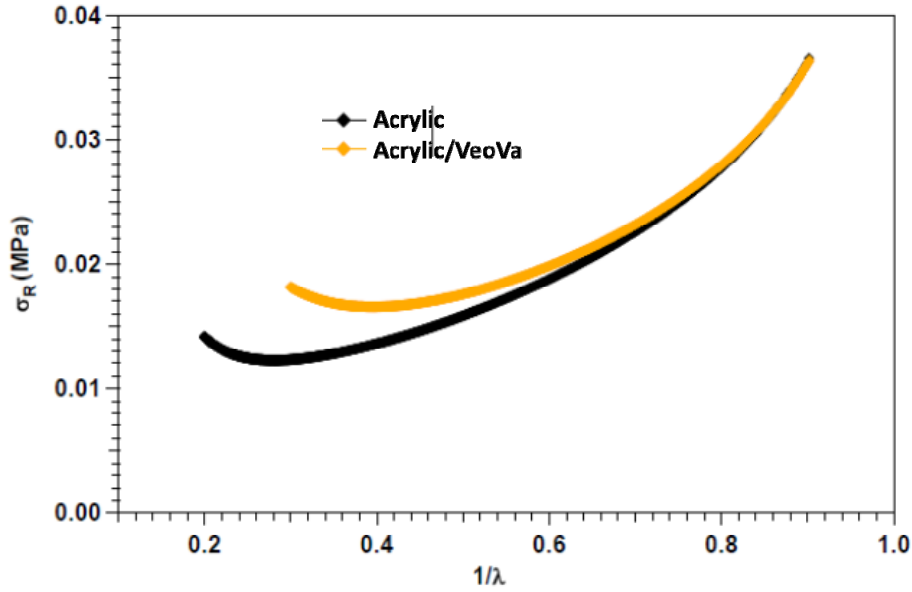


Figure 4: Tensile Test results (σ_R as a function of $1/\lambda$).

The C_{soft} , C_{hard} , λ_{hard} and $C_{\text{soft}}/C_{\text{hard}}$ parameters can be obtained from this method (Table 1).

Table 1. Large Strain properties of the PSA.

	Acrylic	Acrylic/VeoVa
C_{soft}	0.030	0.028
C_{hard}	0.012	0.016
λ_{hard}	3.5	2.5
$C_{\text{soft}}/C_{\text{hard}}$	2.5	1.75

On the basis of the higher C_{hard} value measured for the vinyl ester modified system, it appears that the VeoVa monomer allows a tighter cross linking than an all acrylic without losing its adhesive properties (possibly due to improved adhesive/substrate interactions) and predictably the tighter cross-linking is consistent with the longer shear resistance time.

Enhancing the performances of WB Acrylic PSA

As a result of the high cohesive strength and improved water whitening resistance brought by the hydrophobic vinyl ester, new latexes were prepared. Thanks to a slight process variation and the use of copolymerizable surfactant, high solid ($> 60\%$), low viscosity ($< 500 \text{ mPa.s}$) VeoVa modified WB Acrylic PSA could be prepared.

The adhesion and cohesion values measured for the base polymer and its tackified version are shown in Figure 5. From this graph, it appears that the addition of the tackifier has a very marginal effect on the adhesion to Stainless Steel, yet, a significant improvement of the peel on the Low Surface Energy substrate is measured. Thanks to the outstanding cohesive strength of the pure polymer, the PSA maintains very high shear strength even in the presence of 20 phr of Snowtack® SE 780G.

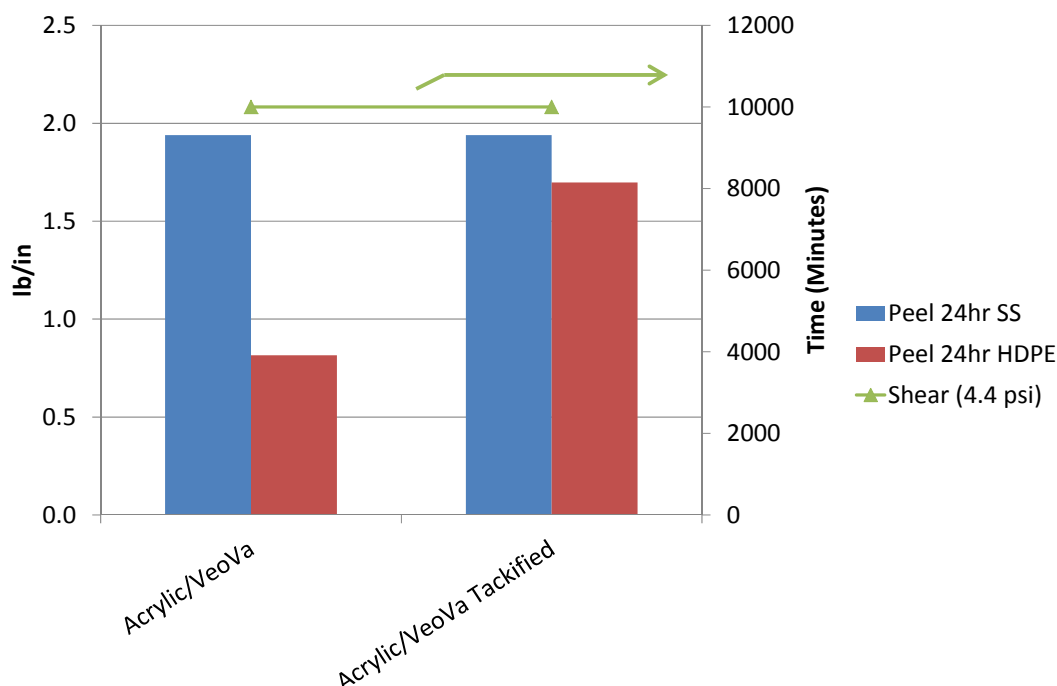


Figure 5: Peel and Shear of pure and tackified WB Acrylic/VeoVa PSA.

Good resistance against water whitening is a key feature in many PSA applications. The improvement brought by the hydrophobic vinyl ester can be evidenced through Delta Opacity measurements performed after direct exposure of the PSA into water at 23 °C for a prolonged period (48h). Figure 6 shows the excellent water whitening resistance achieved with the pure and tackified hydrophobically-modified PSA. This prototype is compared with a pure and tackified (20 phr Snowtack® SE 780G, Lawter) commercial benchmark known for its good resistance against water whitening.

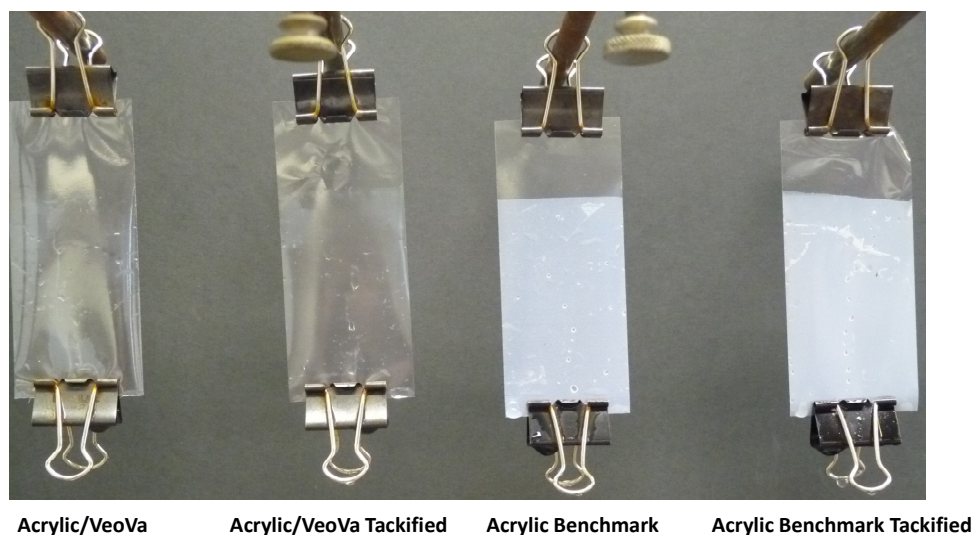


Figure 6: Water Whitening Resistance after 48h of direct exposure in water.

Synthesis and characterizations of the Vinyl Ester PSA

In light of the interesting properties obtained with VeoVa 10 in PSA applications and thanks to our access to softer hydrophobic vinyl ester ($T_g \sim -40$ °C), which can be considered as an alternative to soft acrylates, we have developed a new class of PSA materials³ based predominantly on a combination of vinyl ester monomers (Table 2). Our most recent advances in this field have enabled us to prepare new WB PSA showing high peel strength on polar and LSE substrates together with outstanding shear strength at room temperature as well as at high temperature. Interestingly enough, these materials seem also to perform well under humid environment (see Table 3). On the basis of these properties, these WB PSA position themselves as high performance products possibly finding a fit for Technical Tape applications where a good deal of SB Acrylics PSA are still currently used.

Table 2: Latex characterizations of Vinyl Ester PSA

Latex	Solid Content (%)	Particle Size (nm)	Viscosity (mPa.s)	pH	T_g (°C)
Vinyl Ester PSA #1	54	200	400	4.0	-25
Vinyl Ester PSA #2	48	310	< 200	2.0	-15

Noteworthy, a new bio-based softer Vinyl Ester ($T_g = -70$ °C), currently under development, has also been tested in these systems revealing similar performance levels. In parallel, a new and optimized PSA based on 89 wt% of VeoVa EH, 10 wt% of VeoVa 10 and 1 wt% of Acrylic Acid (Vinyl Ester PSA #2) was prepared in our laboratory. Thanks to the non-polar character of this polymer, unique adhesion levels can be achieved on LSE materials (see Table 4).

Table 3: PSA properties of Vinyl Ester PSA #1 (tested at 50 gsm on 50 μ PET)

PSA Property	Units	VE PSA #1
Stainless Steel		
Peel 20 min.	lb/in	2.3
Peel 24 hr.	lb/in	3.1
Loop Tack	lb/in	2.0
Shear (4.4 psi)	min.	> 10.000
Shear (2.2 psi, 65 °C)	min.	> 10.000
SAFT (2.2 psi)	°C	> 205
Peel 35 °C – 90% RH SS 7 d/substrate	lb/in	3.7
Peel 35 °C – 90% RH SS 7 d/laminate	lb/in	3.8
Glass		
Peel 24 hr.	lb/in	2.9
HDPE		
Peel 24 hr.	lb/in	2.3

Table 4: PSA properties of Vinyl Ester PSA #2 (tested at 50 gsm on 50 μ PET)

PSA Property	Units	VE PSA #2
Stainless Steel		
Peel 20 min.	lb/in	2.5
Peel 24 hr.	lb/in	2.6
Loop Tack	lb/in	2.5
Shear (4.4 psi)	min.	3500
Glass		
Peel 24 hr.	lb/in	2.7
HDPE		
Peel 24 hr.	lb/in	3.9
LDPE		
Peel 24 hr.	lb/in	2.9
PP		
Peel 24 hr.	lb/in	3.0
Teflon		
Peel 24 hr.	lb/in	1.8
PVF		
Peel 24 hr.	lb/in	3.8

Conclusions

In this work, the fundamental investigation of the large-strain mechanical properties and adhesive properties of VeoVa modified acrylic WB PSA have enabled us to better understand the effect of the vinyl ester on the adhesion/cohesion balance of the PSA material. On the basis of these benefits and thanks to the improved water resistance brought by this highly hydrophobic monomer, we have been able to prepare high solids, low viscosity tackified WB PSA delivering high adhesion to HDPE, high shear and excellent water whitening resistance.

Our recent progress in Vinyl Ester PSA have enabled us to prepare new materials showing very good adhesion levels on multiple substrates combined with outstanding cohesion levels, high temperature and humidity resistance. On the basis of this set of properties, it is likely that these materials could start competing with solvent-borne acrylics used in Technical Tapes applications. Finally, non-polar polymers based on hydrophobic vinyl esters have been developed and show unique adhesion levels on the most difficult to adhere substrates.

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