

PRIMERLESS REMOVABLE ADHESIVES

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Introduction

Removable adhesives are increasingly being used in many specialized tape and label applications. These adhesives are said to be removable when the pressure-sensitive material can be removed without facestock failure or significant residue being left behind after removal. These adhesives are comprised of many different chemistries and carriers that deliver a range of performance profiles that are needed due to the large number of application conditions, facestocks used and end use substrates.

Because the adhesion level of these materials is engineered to be very low, anchorage (or adhesion) to the facestock can be a problem. This is generally overcome by the use of a primer coating which adds cost and complexity to the structure. Some facestocks can be purchased pre-primed with a higher energy coating. Many times, a primer is coated and dried either in-line with the adhesive coating or as a separate pass on the coating equipment. Some of the most effective primers are permanent Pressure Sensitive Adhesives (PSAs) and this adds another additional layer of complexity. If the primer is tacky, it cannot be rewound in a self-wound manner. Another means of priming is to coat a non-pressure sensitive material on a facestock that has exceptional specific adhesion to the removable adhesives. This is usually the approach whenever the primer has to be applied in a separate pass and a primed facestock rewound prior to coating the adhesive. Often these are materials that are very similar to the chemistry of the adhesive. Furthermore, when the primer is applied to a porous face stock in a fluid state, it can flow into the facestock to some degree and when set, can form very strong bonds due to entanglements. Hence, anchorage is improved. Either way, the cost and complexity of the system are impacted by the use of a primer to promote adhesion to the facestock.

In Figure 1, the residues on stainless steel panels are shown after performing a peel test on an adhesive that was coated on to primed and unprimed facestocks. Both samples were heat-aged at 50°C for one week before peeling.



Figure 1: Residues on Stainless Steel Panels

To further illustrate the need for priming, two different adhesives were aged on a stainless steel substrate as a function of time. Even though there is a lower peel and higher peel adhesive, both transfer to the substrate regardless of dwell time. As can be seen in Table 1, priming is an effective means of improving anchorage.

Table 1: 90° Peels of Primed and Unprimed Adhesives

Stainless Steel Peels (oz/in)	20 Min Room Temp		24 Hr Room Temp		1 Week Room Temp		1 Week 50 °C	
	Peel (oz/in)	Failure Mode	Peel (oz/in)	Failure Mode	Peel (oz/in)	Failure Mode	Peel (oz/in)	Failure Mode
PSA 1 unprimed	3.6	AFB	4.4	AFB	5.8	AFB	6.4	AFB
PSA 1 primed with Primer 1	6.0	A	7.4	A	6.3	A	8.2	A
PSA 2 unprimed	6.8	AFB	8.9	AFB	11.0	AFB	6.8	AFB
PSA 2 primed with Primer 1	13.3	A	16.4	A	15.3	A	12.9	A

A = Adhesive Failure, AFB = Adhesive from backing failure.

Primerless Approach

In cases where the facestock of interest is porous, improved anchorage could be achieved with just a single pass adhesive if the adhesive would flow in the pores. Removable adhesives typically have very high cohesive strength and relatively little cold flow, so when they are transfer coated, only a very minor portion will flow into the pores. One approach to alleviate this problem is to add a material that will flow into the pores while coating, yet have very little cold flow in its end use. Materials that are either thermoplastic or display some crystallinity have the potential of being of lower viscosity in a molten phase yet rigid when in a glassy or crystalline state. Because the coating of most pressure sensitive adhesives requires heat, it is possible to identify a material that undergoes a phase transition between the temperature a web would reach during the coating process and ambient conditions. Moreover, it is highly desirable that this material remain as a separate phase from the bulk of the adhesive if this desired phenomenon is to be maintained.

To examine this phenomenon in more detail, samples with and without a thermoplastic filler were prepared and transfer coated onto paper by sending the laminate through a hot nip. Afterwards, cross sections were prepared by a cryosectioning and the surfaces were imaged by scanning electron microscopy.

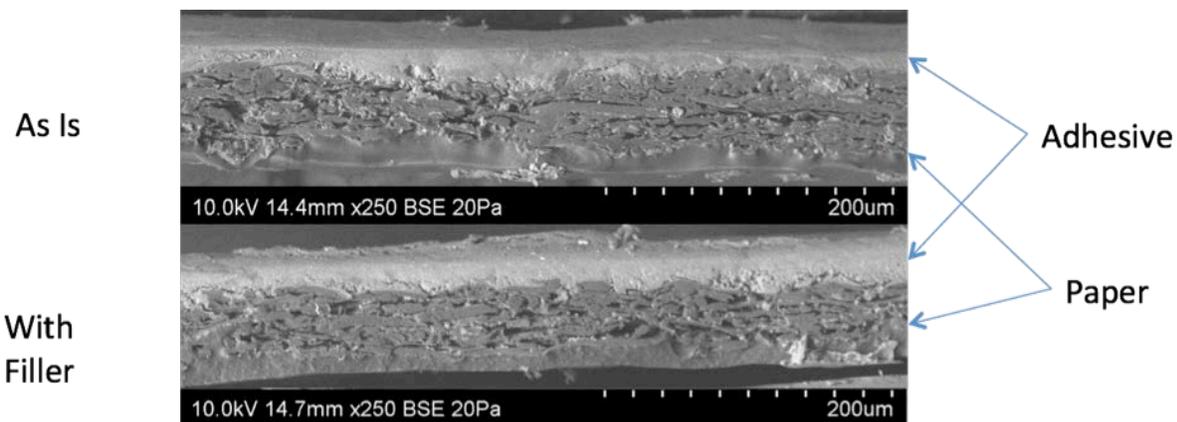


Figure 2: Micrographs of Filled and Unfilled Adhesives

The top half of the figure is an image of the neat PSA whereas the bottom contains 30% of a thermoplastic filler. Because the filler is a relatively molten, low viscosity material when nipped, it is more apt to flow into the pores of the paper. This is seen as the rougher interface in the lower image. Upon additional testing, anchorage was clearly improved with the addition of the filler.

Historically, formulations have been identified that achieve this effect by adding wax to the adhesive¹. In this case, relatively low levels of wax were used and the authors noted the improved anchorage and speculated that it was associated with flow into pores. Waxes are of low surface energy and low viscosity when in the molten form. Consequently, they can be added at low levels to reduce adhesion since thermodynamically, they should be driven to the surface. This could also limit how much material is available to flow into pores because higher levels of wax might overwhelm the surface of the adhesives to such an extent that too much adhesion is lost.

In recent years, The Dow Chemical Company has been able to economically disperse higher molecular weight polymers through use of its BlueWave™ technology.² This is a patented process for mechanically dispersing higher molecular weight polymers while achieving lower particle size. Consequently, many thermoplastic materials can now be prepared as dispersions that historically were not commercially available. Having a wider array of materials also permits one to better tune the finished material to the needs of the application.

Consider the steps that do occur in a transfer coated process. First, a material is coated onto a release liner, dried in the oven, and once it exits the oven, passes through a nip where it is then transferred to the facestock. In certain cases, paper webs are remoistened in order to minimize curl. In other words, there is plenty of opportunity for the web to cool once it exits the oven. Hence, any formulation that extends the open time of the molten filler material is advantageous.

Phase transitions can readily be followed by differential scanning calorimetry (DSC), a technique where heat flow is monitored while ramping temperature at a controlled rate. In Figure 3 and Figure 4, the thermograms of a water-based acrylic formulated with a dispersed wax are present. In both figures, the phase transition of the wax is detected around 80°C and there is only a few degrees difference between the melt and recrystallization temperature. This suggests that the wax will rapidly harden when cooled.

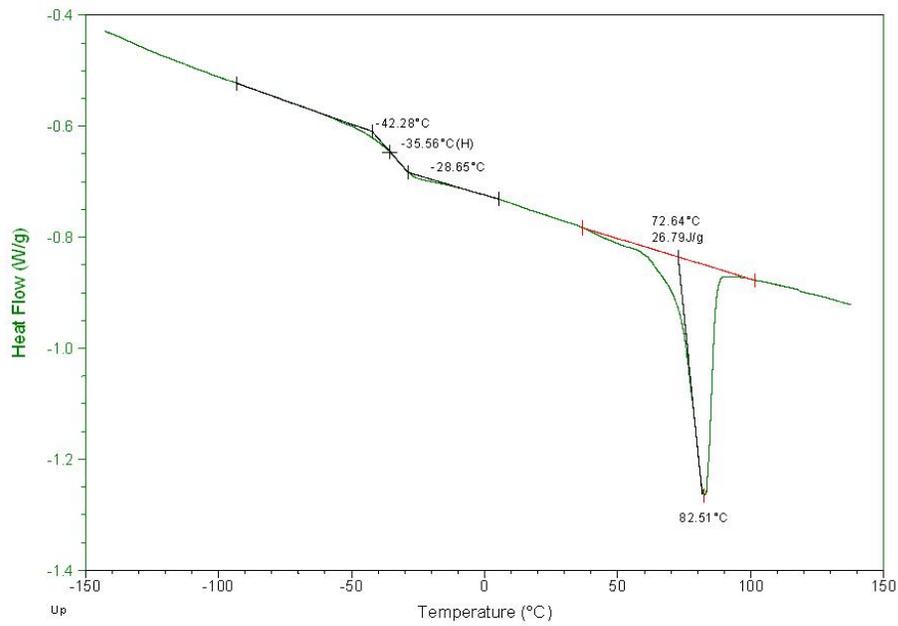


Figure 3: Thermogram: Wax added to PSA

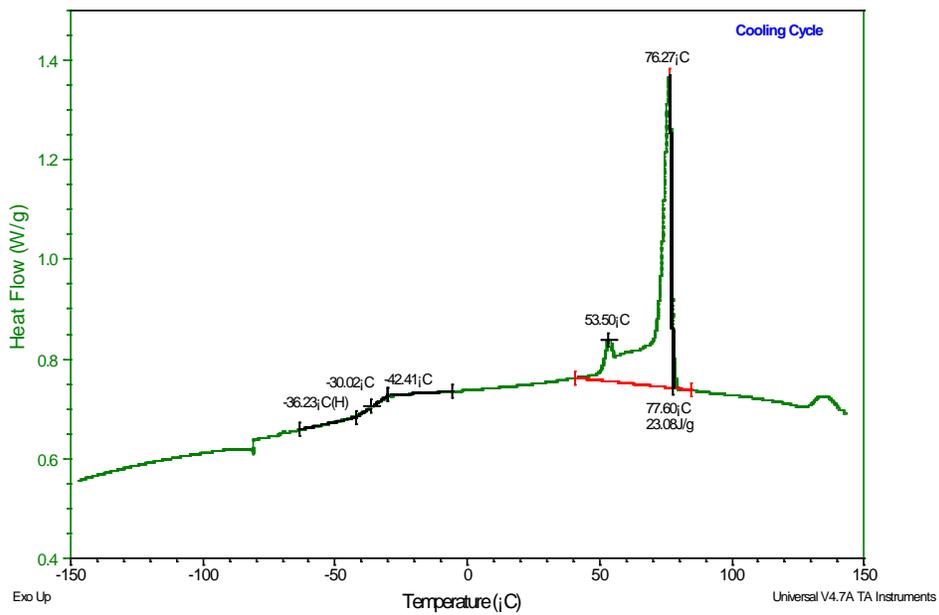


Figure 4: Thermogram: Wax added to PSA; cooling cycle

By carefully selecting the raw materials of the hard filler phase, the recrystallization temperature can be depressed, thereby extending the open time as it cools. As an example, consider the case of a dispersed polyethylene polymer. In Figure 5 and Figure 6, the thermograms of a water based acrylic pressure sensitive adhesive formulated with 30% of a polyolefin dispersion is shown. Once again, the phase transition is above ambient conditions, but in this case, the difference in where the melting is completed and recrystallization begins is around 30°C. At the 10°C rate, this corresponds to 3 minutes in real time. Because the time for the web to travel through the oven and nipping point is only a few seconds, this difference may even be greater in real life applications.

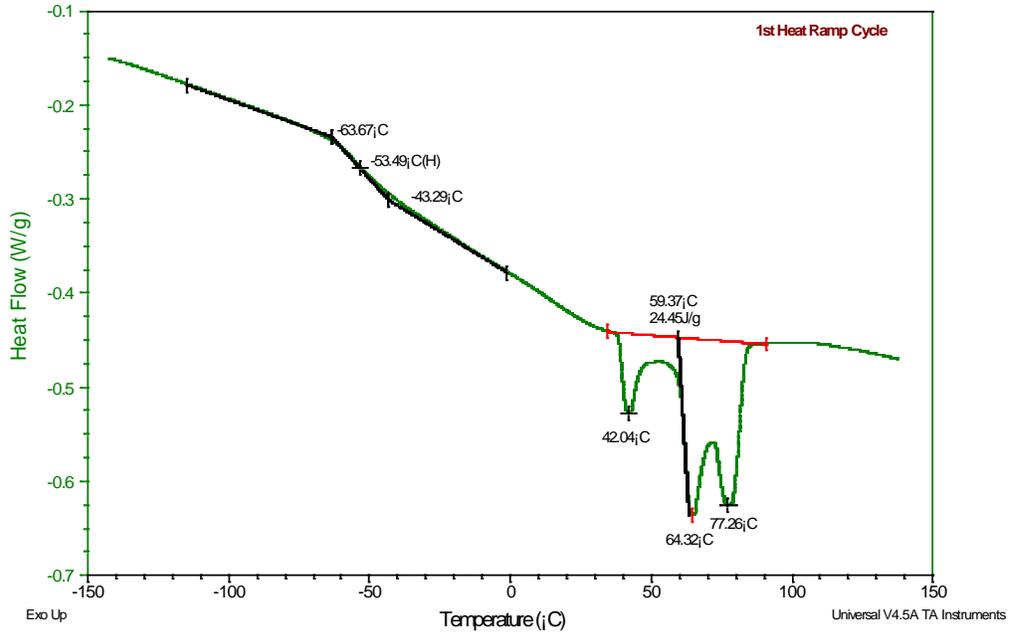


Figure 5: Thermogram: Filler added to PSA

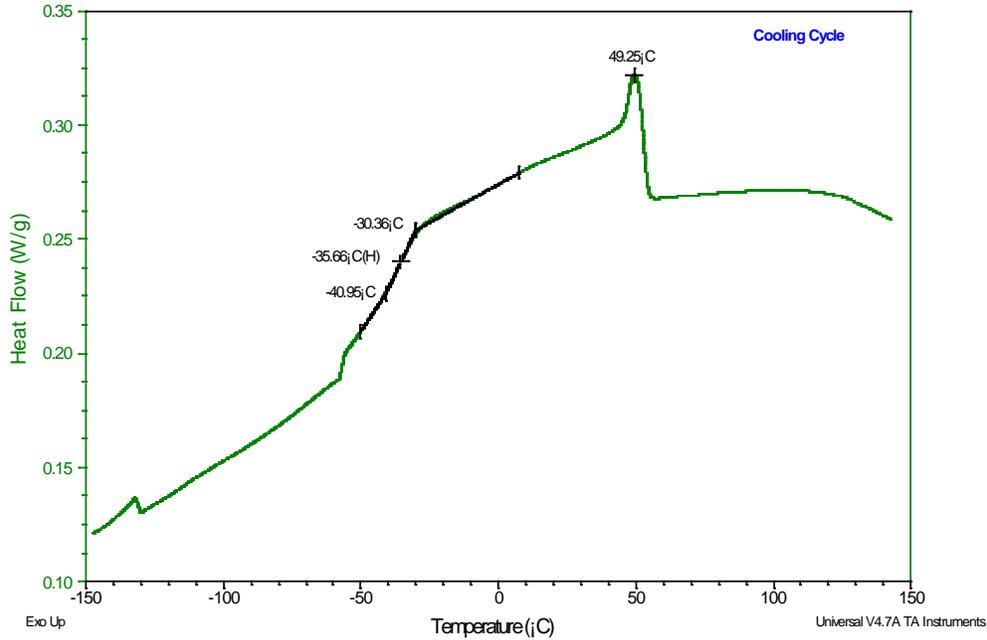


Figure 6: Thermogram: Filler added to PSA; cooling cycle

Adhesive Performance

In this study, two adhesives, PSA1 and PSA2, were formulated with various levels of Filler1, as alternatives to priming paper. Other types of primers were also investigated. To prime samples, a binder, Primer 1, was coated onto 60# glossy paper. Adhesive samples were transfer coated from Chemsultants RP-12 release liner to glossy paper and dried in an 80 °C oven for five minutes. To facilitate a failure mode change from AFB to Adhesive during adhesion testing, samples were passed through a 225 °F laminator at approximately 12 feet/minute after draw downs.

During our initial experiments, peel was measured at designated times – twenty minutes, one day, and one week – on samples held at standard PSTC environmental testing conditions. In order to accelerate aging and peel build effects, samples were placed in 50 °C oven for one week. The standard PSTC method for measuring 180° peels was used.³

Table 2: Peel Analysis

Stainless Steel Peels (oz/in)	20 Min		24 Hr		1 Week		1 Week 50 °C	
	Value	Failure Mode	Value	Failure Mode	Value	Failure Mode	Value	Failure Mode
PSA 2 coated onto Primer1	15.0	A	21.2	A	22.1	A	17.3	A
PSA2 + 30% Filler 1 with heat lamination	2.8	A	6.0	A	4.1	A	4.5	A
PSA 2 with heat lamination	9.3	A	13.5	A	13.5	A	10.6	A/PT
PSA 1 with heat lamination	8.3	A	10.0	A	8.3	A	15.0	M

A = Adhesive failure, PT = paper tear, M = mixed adhesive and cohesive failure.

Adding a hard, thermoplastic filler does decrease the peel of the adhesive, so a lower peel adhesive is also included as a control. Clearly, the filled sample has good removability at all dwell times.

A final measure of anchorage was made by rubbing one's finger back and forth across the surface of the adhesive and qualitatively ranking anchorage. Once again, substantial improvement in anchorage is detected.

Table 3: Subjective Anchorage

Neat Adhesive	1
Neat Adhesive + 30% filler	4
Adhesive on Primed Paper	5

1 = poor, 5 = excellent

Conclusion

Adding a non-compatible thermoplastic filler to a formulation can result in a one part, self priming adhesive. Such a formulation can eliminate steps in the manufacturing process thereby reducing cost and complexity. In addition, recent advances in dispersing technology have made a wider range of thermoplastic materials available for use in water based pressure sensitive adhesives. Hence the thermal properties of any filler phase can be better optimized for targeted end use conditions.

Materials Used

PSA 1	Aqueous Acrylic, very low adhesion
PSA 2	Aqueous Acrylic, moderate adhesion
Filler 1	Aqueous Polyolefin dispersion
Primer 1	Aqueous Styrenated Acrylic

Acknowledgements

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References

- 1) US Patent 5,073,457. Repositionable Adhesive, E. Blackwell (1991)
- 2) Chemical and Engineering News, Vol. 84 (49) page 40 (2006), BlueWave is a registered trademark of The Dow Chemical Company
- 3) Test Methods for Pressure Sensitive Adhesive Tapes, 15th edition ,Pressure Sensitive Tape Council