REPLACING MULTIPLE PSA PROPERTY TESTS WITH A PROBE MATERIAL ANALYZER

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Abstract

A ChemInstruments probe material analyzer (PMA) was used to characterize pressure sensitive adhesives. Standard peel, shear, and tack tests provide fundamental adhesive information, but are not quick and do not provide clear direction when it comes to formulation work. Facestock and adhesive thickness differences are often dominant factors in the standard tests and often do not allow the adhesion differences to show up. In this paper, an example of rubber based adhesive formulation is presented wherein PMA results provide rapid, fundamental, formulation guidance.

Good correlations are possible between traditional test methods and the PMA test method. This provides the prospect of merging multiple tests into a single easy test. Parameters such as dwelling time, probe pressing force, probe speed, and probe geometry can be changed to match the real adhesive application scenario. PMA has shortened the adhesive developing time significantly, especially in rubber/tackifier/oil adhesive systems, and in crosslinked acrylic and silicone systems.

1. Introduction

Formulation of rubber-based pressure sensitive adhesives can consume a lot of time and money because the process usually involves much more than just picking raw materials, blending them and subjecting the mixture to a test. After blending, every adhesive in the formulation matrix must be coated onto some test substrate at a given, well-controlled coatweight and must have uniform surface quality from one sample to the next. Since adhesive viscosity changes as a formulation changes, matching coatweight and coat quality, essential to achieving reliable comparisons, can be difficult to achieve.

Coated substrates are ordinarily subjected to a battery of different tests to ascertain the suitability of the adhesive candidates for the intended application. Typically, in the tape and label industries these tests include stainless steel (SS) peel adhesion, loop tack off SS, and static shear. More often than not, a series of other, application-specific tests are also performed. Examples of the latter include mandrel hold, adhesive extensibility, probe tack or rolling ball tack, dynamic shear, quick stick, T-peel and the like. Since coated substrates must be carefully cut to uniform sizes and prepared for testing, as the number of tests increases, sample preparation time can increase geometrically.

Even with data from a variety of different conventional tests in hand, the way forward to make formulation improvements is not necessarily straightforward because the physical properties of the coated substrate are superimposed on the adhesive's properties and because numerical test results do not 'paint a picture' of what's happening inside an adhesive.

The probe material analyzer (PMA) test offers formulators a faster and more transparent way to evaluate adhesive properties by vastly simplifying sample preparation, eliminating adhesive substrate effects and providing a visual picture of how the molecules in an adhesive respond to stress. The PMA test, alternately known as a Texture Analyzer test, has been previously described in the literature (1, 2, and 3) for measuring adhesive properties.

A PMA measurement typically consists of two steps: the bonding step in which a probe attached to a load cell is pressed against the adhesive, and a second step in which the probe is separated from the adhesive. The probe tip which makes adhesive contact can be made from any number of materials such as polypropylene, polyethylene, SS, glass, etc. Probe tips can also be configured with practically any geometry, but the most common are flat and circular or hemispherical.

PMA test parameters that can be varied include insertion speed, the force at which insertion is stopped, static dwell time after insertion, compressive force needed to trigger probe withdrawal, probe withdrawal speed, and withdrawal travel distance. One should do some up-front work to determine what test parameters work best for a given adhesive type and application. Some general considerations about setting test parameters:

Insertion speed: Slow insertion speeds can simulate applications where generous bonding times exist such as when the adhesive product will be applied by hand or when one suspects that adhesive creep will play a large role in the bonding process. On the other hand, rapid insertion could simulate the impact of a rotary die cutting blade on the adhesive or a slitter knife slicing its way through product. If the final adhesive product will be applied at high temperature, one might choose to use a slow insertion speed because adhesives become softer at high temperature and creep faster.

Insertion force or insertion distance: If the adhesive will experience a heavy rolldown, or high application force during use, one might choose a large insertion distance or a high insertion force. When testing stiff adhesives, one may want to use a high insertion force to ensure that the probe makes good contact before the retraction phase begins. If one were testing a PSA for a fly catching strip, one would probably choose a low insertion force or distance for the obvious reason that an insect cannot apply a large force to the adhesive.

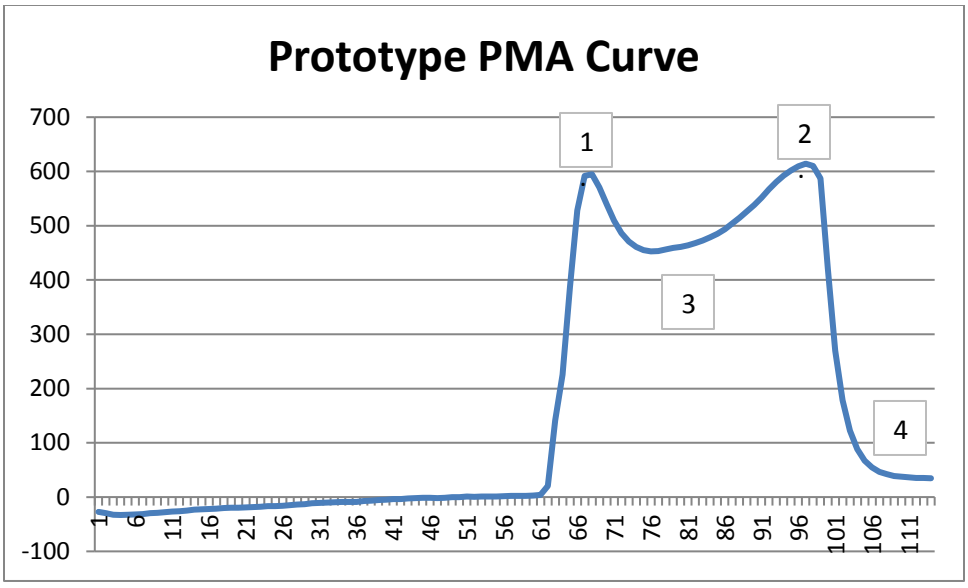
Insertion dwell time: Dwell times can range from 0 seconds up to many minutes. If the final adhesive product will likely dwell for a long time before experiencing any stress, a longer dwell time will give the best simulation. Alternatively, if one is developing, say, a box closure tape, the final product will experience stresses immediately after application and the PMA probe dwell should be set to 1 second or less.

Retraction speed: Since low speed correlates to high temperature, and vice versa, one would choose high retraction speed to simulate removal of a freezer tape from a package or the unwind force of a construction tape being used outdoors. High speed retraction would also be used to facilitate prediction of high speed die cutting performance of labels. A mouse pulling his foot out

of an adhesive rodent trap, or the shear performance of a mounting tape under very low load would be best predicted by using low PMA retraction speeds.

Retraction distance: In most cases, the retraction distance setting is a matter of convenience; once one knows, for example, that all samples will release from the probe at less than a certain distance, setting that distance as the retraction distance will stop the test sooner and save time. There may be circumstances however where one wanted to extend the adhesive a certain distance while remaining attached to the probe and then hold, or where one wants to cycle the adhesive between compression and extension.

Four numbers are commonly used to parameterize a PMA test graph. To illustrate them, consider the following PMA curve:



The test depicted here begins at the left and proceeds to the right. Positive Extraction of the probe from the adhesive mass begins where the curve passes from negative values of force (in grams, on the Y-axis) to positive values. The X-axis here represents passage of time.

1. This is the 1st peak. The height of this peak relates primarily to adhesive tack.
2. This is the 2nd peak. The height of this peak relates to the degree of crosslinking, or extensibility, of the adhesive. (In SBC rubber-based adhesives which are usually not chemically crosslinked, the term crosslinking refers to how much reinforcement is generated by the styrene endblocks.)
3. The area under the (positive) retraction portion of the curve represents the amount of work expended to elongate and separate the adhesive from the probe and has been correlated with peel adhesion and tack.
4. When the adhesive is completely separated from the probe, the force drops to zero. The distance (or time) from the beginning of positive retraction to complete separation from the probe is a measure of the adhesive's shear strength.

The objective of the work described here was to develop a general purpose, hot melt, label adhesive formulation using low cost, locally available raw materials. The coating, converting,

and on-product performance of the new formula needed to approximately match those of two commercial adhesives already in use by our client.

2. Experimental

Sample Coating

Adhesives were melted in an oven at 165^{0}C, coated at 18 gsm on easy release siliconized paper using a ChemInstruments LC-100 drawdown coater and then immediately laminated to 2 mil BOPP film provided by the customer.

Adhesive Mixing

Mixing of adhesives in solvent was accomplished by dissolving the rubber components in toluene at 28.57% solids on a jar rolling machine, then adding the remaining components and enough toluene to arrive at 50% solids solutions, and again rolling the container for several days.

Mixing of adhesives as hot melts was done as 750 gram batches in a 1 liter, Read Standard sigma blade mixer. The procedure was as follows:

1. Heat mixer oil to 400*F
2. Add all rubber, antioxidants and ~1/4 of solid tackifier and mix 20 minutes
3. Add ~1/4 solid tackifier and mix 20 minutes
4. Add ~1/4 solid tackifier and mix 20 minutes
5. Add remainder of solid tackifier and mix 20 minutes
6. Add oil and, if applicable, filler and then mix ~15 minutes.

The mixing chamber was purged with nitrogen after each opening of the lid. 400*F was the set point temperature for the mixer oil; actual adhesive temperatures in the mixer did not exceed 340*F.

Sample sizes

Stainless steel (SS) Peel Adhesion test strips were exactly 1” wide strips cut from cast adhesive samples using a razor blade sample cutter.

Static Shear and Edge Lift test strips were cut to ½” width using a razor blade sample cutter.

Sample conditioning

All test strips were conditioned at least 24 hours at 50% RH / 73^{0}F prior to testing.

Sample testing

Peel Adhesion
Peel adhesion was tested according to the ASTM D 3330 method. Peel adhesion testing was performed on a ChemInstruments AR-1000 Adhesion Release Tester with the EZ Lab software

program. Exactly one (1.0) inch wide samples were applied to a standard stainless steel substrate at a rate of 24 in./min. with a 4½ pound rubber covered roller according to the method. The tape was then peeled from the substrate at a 180° angle at 12 in./min. after a dwell time of less than one minute. The force required for removal was measured, averaged, and the mode of failure noted. Three replicates of each sample were tested.

PMA

PMA behavior was measured by using a ChemInstruments PMA-1000 Probe Material Analyzer. The probe was flat, polished SS with diameter of 3/16 inch. Before each test the probe was wiped clean using a lint free cloth dampened with toluene. Samples were prepared as follows: Exactly 10g of each adhesive dissolved in toluene (@ 50% solids) was poured into a 3" diameter aluminum dish and then dried 64 hour @ 50*C in a circulating air oven.

The Al dishes were taped to the rigid platform below the PMA probe using double coated mounting tape. During each test, finger pressure was also used around the perimeter of the Al dish to help hold it down in place during the retraction of the probe.

Probe insertion speed was set at 0.25 inch/minute. Upon reaching 25 grams of insert force against the adhesive surface, the probe is held steady for 3 seconds and then retracted from the sample at 40 inches/minute. The force required to separate the probe from the adhesive surface was measured as the probe retracts. A fresh location on the adhesive in the dish was used for every test. Two or three replicate tests were performed for each sample.

All forces were recorded in grams. Our PMA load cell generates 400 data points per second. When the data is graphed or stored to an Excel file, the software averages every 8 sequential points in a sequence, so the 400 data points generated in 1 second become 50 data points per second on the graph or in an Excel file. The graphs depicted in this paper were generated from the stored Excel file data.

Static Shear

Static shear was tested according to the ASTM 3654 test method. Shear was tested on a ChemInstruments RT-30 Shear Tester. A 0.5 inch by 0.5 inch sample was applied at room temperature to a 2" by 3" panel with a 4½ pound rubber covered roller at a rate of 24 in./min. according to the test method. An aluminum clip to evenly distribute the applied load was attached to the free end of the sample. The panel with the sample was placed in the shear test stand. After a dwell time of one minute a 500 g mass was hung from the clip. As the weight was positioned on the sample, timing began. When the sample slipped from the panel, the timer automatically stopped. The time and the mode of failure were recorded. Three replicates of each sample were tested.

Mandrel Hold

Mandrel hold ('Edge Lift') was measured using ½" wide strips of test labels on the exterior surface of glass rods (mandrels) with 8mm diameters provided by our Client. The mandrels were solvent cleaned using MEK and lint-free KimTech wipes and then air dried 1 hour prior to application of label test strips. The liner was removed from the label and it was applied by wrapping it around the test tube by hand so the ends nearly touched each other. Care was taken to not entrap air under the label. The surface of the label was then gently rubbed with the finger

to apply uniform pressure across the entire surface of the label. The label was then allowed to rest in a 73°F, 50% RH environment for 16 and 40 hours. At the end of the prescribed time periods, the labels were visually inspected for signs of lifting, tunneling and/or flagging using a 10X hand magnifier. Three replicates of each sample were tested.

Test Conditions
All tests were conducted at 73 ± 3°F and 50 ± 5% Relative Humidity.

3. Approach and Limitations

In the interest of saving time and staying within the project budget, we chose to compound experimental formulas from solvent and only resort to sigma blade mixing at the last step. We also decided to use PMA testing to guide selection and relative amounts of the raw materials in experimental formulations. Traditional peel, mandrel hold, static shear and viscosity tests were only performed at the last step when evaluating final formulas compounded in a sigma blade mixer.

The starting formulation was based on past experiences with hot melt rubber PSA formulations for adhesive tapes. That is, the formulation would have about 1/3 rubber, 1/2 solid tackifier, 1% antioxidants, and the balance oil or liquid tackifier. Before beginning the project we planned to actively seek expert advice from key vendor contacts.

It was expected that we would complete the project in 6 steps, to include:

1. Benchmark the performance of the two current adhesives.
2. Identify SBS rubber(s) to be used
3. Screen oil candidate raw materials
4. Screen solid tackifier candidates
5. Optimize rubber, oil and tackifier ratio
6. Use sigma blade compounding to verify the new formula and to test filler candidates

Our customer wished to replace both control adhesives with 1 formulation. Further, starting with a list of potential raw materials that we provided, our customer would specify which rubbers, oils, tackifiers, fillers and antioxidants to include based on price and local availability.

4. Results

Step 1: Benchmark current products manufactured with control adhesives

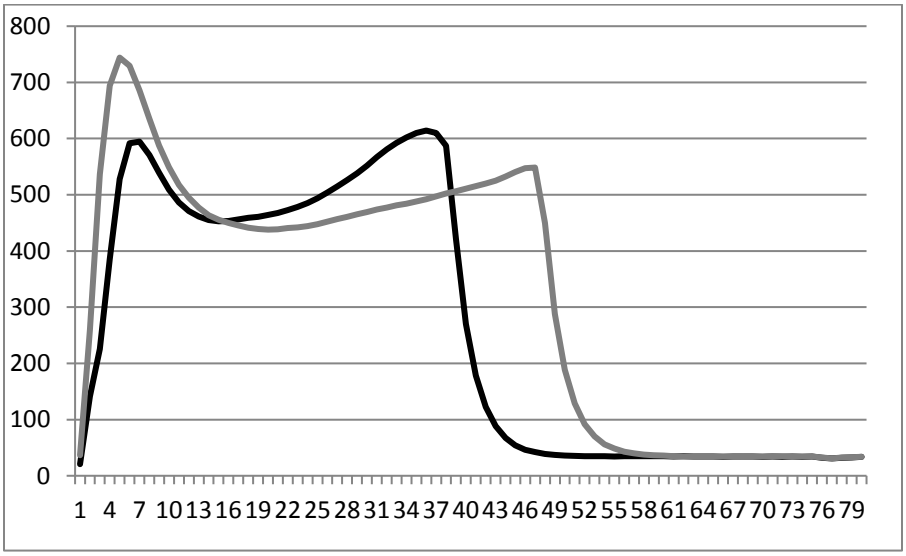
The customer provided blocks of two hot melt, control adhesives which they used in current label production. Samples of each were dissolved in solvent for PMA testing and they were hot

melt coated on 2 mil, customer supplied BOPP for peel, shear and mandrel testing. The customer also provided one control adhesive pre-coated on 2.6 mil BOPP and the other control adhesive pre-coated on 2.6 mil paper. These pre-coated and in-house coated samples were subjected to peel adhesion, static shear, mandrel edge lift tests with the following results:

Step 1. Benchmark Test Summary Table

Adhesive Name	180 SS Adhesion (Lb/in)	Static Shear .5"x.5"x500g (min)	Mandrel Edge Lift (on 8mm glass rod)	PMA Probe Tack Peak (grams)	PMA Probe Tack Average (grams)	PMA Probe Tack Work (mJoule)	PMA Probe Tack Distance (inch)	Brookfield Viscosity 350*F (cps)
Control 1 adhesive 2.0 mil BOPP Coated in-house	3.90	223	1 mm	432	319	48	0.90	6,350
Control 1 adhesive 2.6 mil BOPP Customer coated	3.45	2,585	no	- - -	- - -	- - -	- - -	- - -
Control 2 adhesive 2.0 mil BOPP Coated in-house	5.30	1,499	no	568	391	84	1.25	7,750
Control 2 adhesive 2.6 mil paper Customer coated	*sample tears*	2,344	no	- - -	- - -	- - -	- - -	- - -

The darkest PMA curve is Control 1 and the grey curve is Control 2:



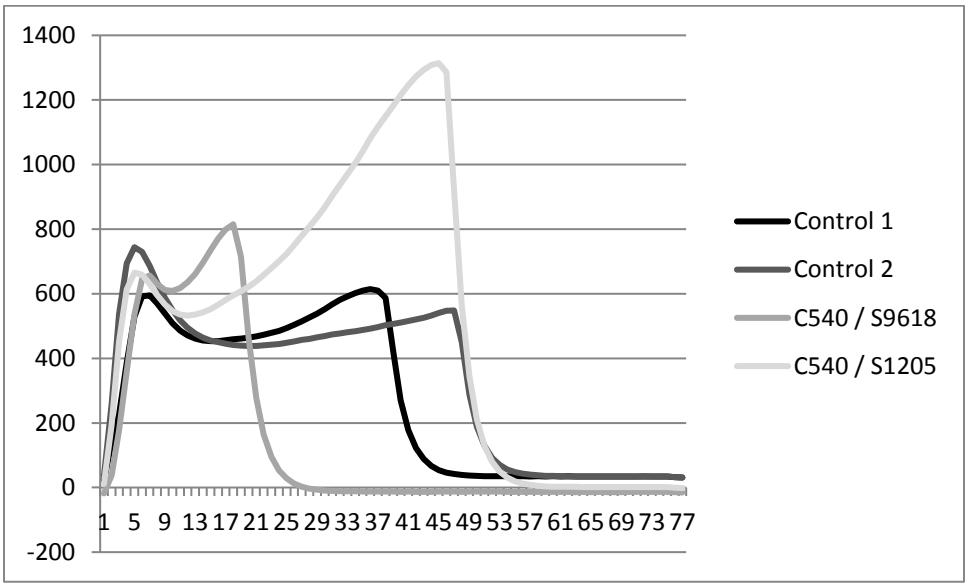
Step 2: Solvent formulation to identify best SBS rubber(s)

Our screening formula was 32% rubber, 53% solid tackifier, 14% oil and 0.5% each of a primary and secondary antioxidant.

After conferring with a technical expert at the rubber supplier, we decided that the rubber component would be a blend of two different rubbers: C-540, a linear, SBS polymer with ~40% styrene combined with S-1205 SSBR random copolymer containing 25% styrene, or C-540 combined with S-9618 multi-arm SBS polymer containing 31% styrene and ~65% diblock. The idea here is that C-540 has a low softening point and imparts cohesive strength whereas S-1205 or S-9618 impart substrate wetting, tack and tackifier compatibility. The amount of tack and adhesive elasticity can be easily adjusted by varying the relative amounts of the two rubber components. Our starting point C-540 to S-1205 ratio was 1/1 and C-540 to S9618 ratio was 3/5.

The solid tackifer for this stage was a gum rosin ester named G-85 and the oil used was L-2000. Irganox 1330 and Irgafos 168 were our customer designated antioxidants.

The adhesives were formulated and PMA samples prepared. The PMA test results for the two new adhesives are shown superimposed over the Control adhesives' curves:



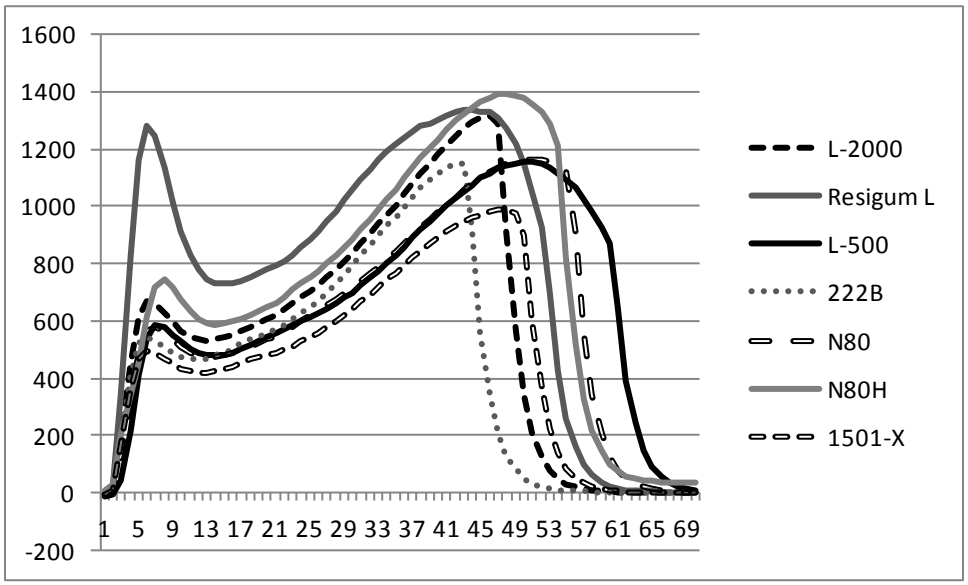
From this PMA comparison we decided to discontinue investigation of S-9618 because we reasoned that even if we had used a C-540/S-9618 ratio of 0/1, we would not be able to achieve the adhesive elongation exhibited by the Controls. On the other hand, our C-540/S-1205 combination was already a good elongation match to the Controls and could easily be adjusted up or down as needed. The peak heights of the C-540/S-1205 formula were also already capable of matching the Controls and the 2nd peak in particular hinted that our new adhesive had the potential to deliver superior static shear.

Step 3: Solvent formulation to identify best oil

Our screening formula was 32% rubber (16% C-540 and 16% S-1205), 53% solid tackifier (G-85), 14% oil, and 0.5% each of Irganox 1330 and Irgafos 168

We were asked to evaluate 6 different oils: H-2000 and H-500, 222B, N80, N80H, and 1501-X. In addition, we included a liquid rosin ester named Resigum L.

The adhesives were formulated and PMA samples prepared. The PMA test results for the seven adhesives are shown here superimposed on each other:

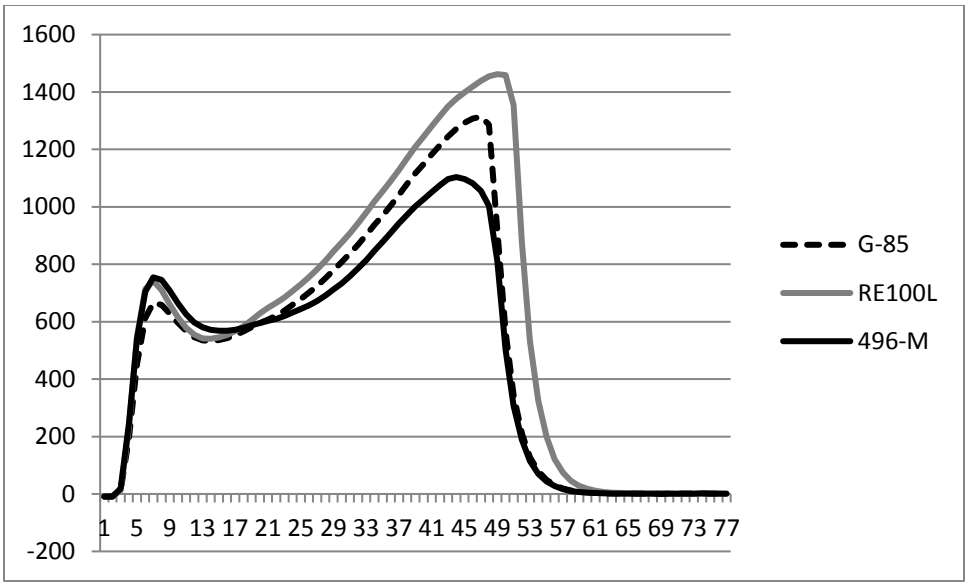


The formulation with Resigum L liquid tackifier clearly stands out by virtue of its high 1st peak, but we could not pursue it in the final formulation because of its high cost in comparison to all of the naphthenic oils. Amongst the latter, the PMA test results were generally similar, but the candidate which exhibited the best combination of 1st peak height, 2nd peak height, elongation, cost and availability was N80H. We elected to continue all further formulation work with N80H on the basis of this PMA chart and the business related factors provided by our customer.

Step 4: Solvent formulation to screen solid tackifiers

In addition to the previously mentioned G-85 tackifer, our customer asked us to examine gum rosin esters named RE100L and 496-M. We used the same general formula as in the previous oil screening step, but here fixed the oil as N80H and varied the solid tackifer.

The adhesives were formulated and PMA samples prepared. The PMA test results for the adhesives with different solid tackifiers are shown here superimposed on each other:



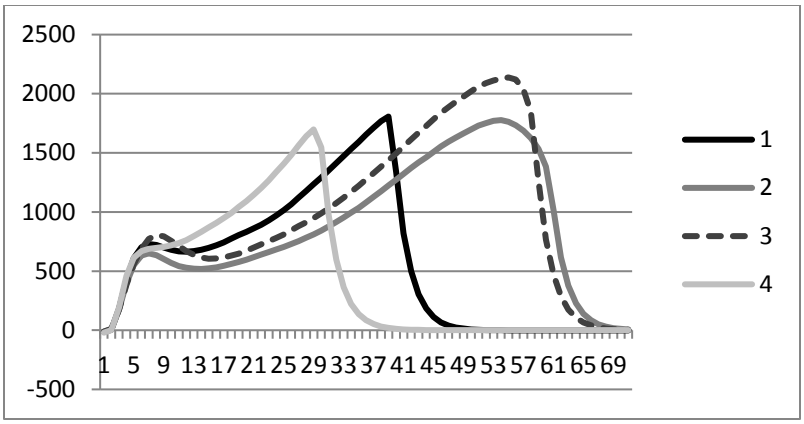
Here, as with oil screening, the PMA chart combined with business information from a purchasing department made our selection of which raw material to carry over to the next stage of formulation development rather easy. In this case we decided to do the remainder of the development with RE100L.

Step 5: Optimize rubber/tackifier/oil ratio

The PMA data obtained in previous steps indicated that our formula was approximately what was needed to match the Control adhesives. We decided to evaluate the following variations from the general screening formula used in the previous steps:

Component	1	2	3	4
SBS rubber	0.16	0.14	0.182	0.208
SSBR rubber	0.16	0.14	0.098	0.112
Tackifier	0.53	0.57	0.57	0.50
Oil	0.14	0.14	0.14	0.17
Irganox 1330	0.50	0.50	0.50	0.50
Irgafos 168	0.50	0.50	0.50	0.50

In this table, “1” is the general screening formula used in previous steps. After these adhesives were compounded, cast in dishes and analyzed for PMA performance, we obtained this picture:



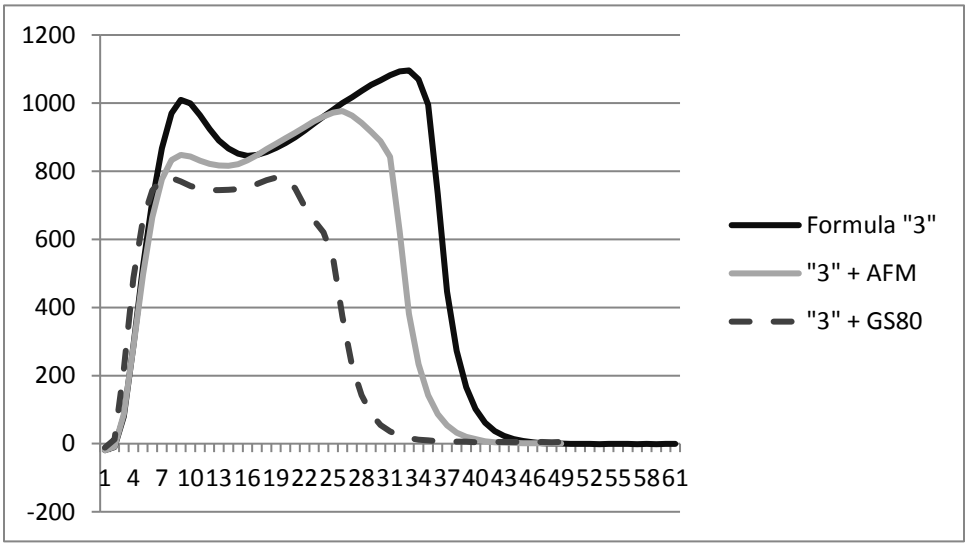
When we take rubber away from "1" and replace it with tackifier, the adhesive has approximately the same 1st and 2nd peaks, but the bulk elongates more when stressed because there is a smaller styrene phase to resist. If we keep the same total rubber as "1" but with higher C-540 fraction, and replace a little tackifier with oil, as in formula "4", the 1st and 2nd peaks are again unchanged, but now the adhesive is incapable of elongating to the original extent. In adhesive "3", the lower total rubber content allows greater elongation in spite of slightly more high strength C-540, while the tackifier increase has caused a modest increase to both the 1st and 2nd peaks.

Step 6: Sigma blade compounding and filler comparisons

Formula "3" was taken to the sigma blade mixer for solventless compounding. Since our customer's Control 1 adhesive contained filler, we also used the sigma mixing step to screen two different fillers: AFM3, a three micron calcium carbonate product, and 2.5 micron Gama-Sperse 80 (GS-80) calcium carbonate. Based on previous experience with filled adhesives in PSA tapes, the fillers were added at 7.9% by weight.

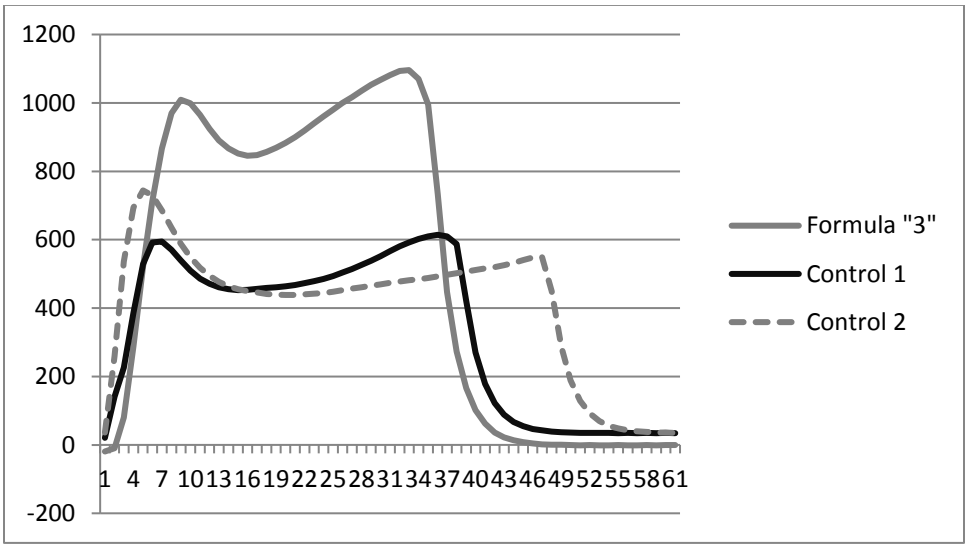
750 gram batches were prepared in a 1 liter sigma blade unit at 100% solids with 340^0F adhesive temperature. Afterward, samples for PMA testing were dissolved in solvent and cast into dishes, while peel, shear and mandrel samples were prepared by hot melt coating.

The PMA differences caused by filler addition are illustrated by the following:



Our interpretation of this is that at a given weight, the finer particle size and narrower size distribution of Gama-Sperse 80 causes more reinforcement than AFM3 and will result in lower tack and peel. The difference could be made up by formulating a given adhesive with less Gama-Sperse 80 than AFM3. If one's objective is cost reduction, however, then AFM3 may be a better choice.

The PMA results for hot melt mixed formula "3" are shown here superimposed over the original PMA results for our customers' Control adhesives:



Based strictly on peak heights, one would expect formula "3" to have higher peel and tack than the controls; but, when adhesive removal work, the area under the curve is also considered, one might expect formula "3" and Control 2 adhesives to have similar peel.

Benchmark testing of peel, static shear and mandrel hold of formula "3" and its filled versions was conducted following hot melt coating at ~18 gsm coatweight on 2 mil BOPP.

Step 6. Benchmark Confirmation Testing

Adhesive	180 Peel Adhesion			Static	Mandrel
Name	0 week	2 Week	4 Week	Shear	Edge Lift
	Unaged	140*F	140*F	.5"x.5"x500g	(8mm
	(Lb/in)	(Lb/in)	(Lb/in)	(min)	Glass)
Formula "3"	4.53	4.74	4.27	10,000+	no
"3" + AFM3	3.44	3.23	3.58	10,000+	no
"3" + GS80	3.10	2.63	2.69	10,000+	no
Control 1 adhesive	3.90	2.43	2.34	223	YES, 1mm
Control 2 adhesive	5.30	4.90	5.12	1,499	no

The initial and aged SS peel adhesions of the new adhesive in both filled and unfilled ("3") form align well with adhesions of the two adhesives it is designed to replace. The static shears of our new adhesives represent a significant improvement over the Control adhesives and none of the new adhesives exhibited mandrel edge lift when bonded to small diameter glass rods.

We profiled the viscosity versus temperature relationship of the new adhesives with the following results:

	Brookfield Viscosity (centipoise)				
Temperature	Formula	Formula	Formula	Control	Control
Temp.*F	"3"	"3" + AFM	"3" + GS80	1	2
280	30,500	21,000	25,000	28,450	50,900
300	14,050	15,750	16,150	17,050	23,200
325	7,325	10,070	8,525	8,675	13,350
350	5,125	4,850	5,525	6,350	7,750
375	3,460	3,975	3,925	4,150	5,700

With viscosities similar to that of Control 1 and somewhat lower than Control 2 adhesives, our new formulas should die coat very well on our customer's hot melt coating lines.

5. Conclusion

We demonstrated that a Solvent/PMA-only approach was capable of quickly and inexpensively generating a label adhesive formula with peel, shear, edge lift mandrel and viscosity performance to match our customers' commercial label adhesives.

6. References

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2. Kilian, L., Lewis, C.M. (2011), "A New Approach to Measuring PSA Cohesive Strength Using a Texture Analyzer" PSTC Tech 34 Seminar Proceedings.
3. Holguin, Daniel, et. al. (2003), U.S. Patent Publication number US20030134033A1

7. Acknowledgements

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