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DIBENZOATES IN PSA'S

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USE OF DIBENZOATE PLASTICIZERS IN PRESSURE-SENSITIVE ADHESIVES

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Abstract

Plasticizers extend the utility of the polymers in which they are used. Despite already having low Tgs, waterborne, solvent and hot melt pressure-sensitive adhesives can utilize plasticizers to enhance performance characteristics. Because of their polarity and range of compatibilities, dibenzoate plasticizers find wide usage in latex adhesives. In recent years, new blends and grades of dibenzoates have been developed to enrich the choices available to the formulator. These choices include a new dibenzoate triblend platform. Little has been published on the use of dibenzoate plasticizers in waterborne pressure-sensitive adhesives. The purpose of this paper is to show how plasticizers function with the soft polymers used in PSAs and to describe ways in which these plasticizers can be used and how they affect performance attributes. The focus of this presentation will be on the newer dibenzoate products.

Background

Plasticizers are normally used in polymeric systems to soften or to improve the processability of the composition. This is the basic definition of a plasticizer, with the caveat that the plasticizer needs to be at least partially compatible with the polymer being used. A measure of the effectiveness of a plasticizer can be the reduction of the glass transition of a polymer; the degree of suppression of the glass transition is also an indication of the compatibility of the plasticizer with the polymer and the other ingredients in the composition. The workability or processability of a plasticized composition may be more important than the actual softening of the polymer in the composition for some applications.⁽¹⁾

The use of plasticizers in pressure-sensitive adhesives (PSA) is well known.^(2,3,4,5) The need for a plasticizer in a PSA certainly is driven by the type of adhesive as well as by the polymer in it. However, waterborne acrylic based PSAs, solution borne PSAs and hot melt PSA's have been known to utilize plasticizers to enhance performance. For example, acrylic-based waterborne PSAs can use plasticizers to:

- Improve the wetting of the substrate and speed of wetting;
- Increase peel strength;
- Reduce the effective softening point of a tackifying resin and the combination will tackify more effectively.

In addition to improving peel, the tack of the adhesive can be also improved. However, there is also the fact that plasticizers will reduce the holding power of the adhesive. Plasticizers will also affect the performance of solution-borne acrylic adhesives in similar manners.

Hot melt PSAs based on block copolymers (styrene types) are also likely to employ plasticizers. In the case of these compositions the plasticizers will be used to control the service type of PSA: to adjust the polymer/resin's overall Tg to meet the Dahlquist criteria for performance (which is true of all PSA adhesives).^(6, 7, 8, 9)

The polymer type dictates which plasticizer will be of most use. In the case of acrylic polymers, polar plasticizers are a good choice. Classically, di-n-butyl phthalate (DBP), diisobutyl phthalate (DIBP), di-2-ethylhexyl phthalate (DOP), or diisodecyl phthalate have been plasticizers of choice.^(3,4) Other plasticizer types including dibenzoates have been known to be used in these types of adhesives. In hot melt PSAs, oils such as aliphatic, cycloaliphatic and aromatic types are employed as plasticizers.^(10, 11) Performance is dictated by compatibility and lack thereof. If a plasticizer is less efficient, more can be added; this is sometimes an advantage if more plasticizer use is desired. The type of oil is selected based on total performance needs.

Polar plasticizers can be used in block copolymer but mostly (with one exception) what is used is some type of oil. A significant amount of literature is published on the use of oils in PSAs but not a lot are available on the use of polar type plasticizers in any PSA.⁽¹⁰⁾ Even less literature is available on the use of dibenzoates in PSAs. With that in mind, the focus of this paper will be on the polar PSA polymers as that is the most likely significant use area for dibenzoates.

The class of phthalate esters has environmental and health concerns. If adequate replacements are available, non-phthalates are the plasticizers of choice. As mentioned earlier, dibenzoates have been used in acrylic PSAs in the past. They are certainly non-phthalates but before that was important they were polar specialty performance plasticizers. As a matter of fact, dibenzoates are the general purpose plasticizers of choice for waterborne adhesives based on polyvinyl acetate homo and copolymers.⁽¹⁾

Historically, dibenzoates have been known since the 1920s. The first patent listing use of dibenzoates in polyvinyl chloride compositions was in the late 1930s. Since then the dibenzoate family has grown. The first two dibenzoates of importance were:

- Diethylene glycol dibenzoate, and
- Dipropylene glycol dibenzoate.

These still are important plasticizers, and blends of the two are commonly used. However, newer blends and other dibenzoates and benzoates have gained in use as they have been developed to keep pace with the industry.

Most recently, two new blends of dibenzoates and a new grade of propylene glycol dibenzoate have been introduced for adhesives and other applications. They are:

- A blend of diethylene glycol dibenzoate, dipropylene glycol dibenzoate and propylene glycol dibenzoate, and
- A blend of diethylene glycol dibenzoate and dipropylene glycol dibenzoate, very rich in diethylene glycol dibenzoate and manufactured for efficiency.

These dibenzoate products have been investigated extensively for use in latex adhesives and the results of those studies are demonstrated elsewhere⁽¹⁾. The purpose of this study is to demonstrate how dibenzoates function in waterborne acrylic PSAs and will focus on the use of the new dibenzoate triblend.

Experimental

Introduction

Two PSA acrylic waterborne polymers were selected to be the basis of the adhesives of this study. One had a Tg of about -20°C and the other was about -40°C. Tackifier dispersions were selected for each evaluation segment. The plasticizer selected for the study was the triblend of dibenzoate plasticizers listed above which is abbreviated 975P. As there are many possible combinations, a DOE (design of experiments) approach was selected to gain a better understanding of how the polymer, resin and plasticizer interact. It is true that initially a screen experiment is often the best approach to start the DOE process. However, based on what is already known about plasticizer use in PSAs it was felt that a mixture design was the best approach.⁽¹²⁾

Design Expert™ 8 made by Stat Ease® was the software selected for the study. A mixture design, Optimal D, quadratic, was selected. The design variables were:

- Polymer: 60 to 100% maximum were the limits selected;
- Tackifier dispersion: 0 to 30% maximum;
- Plasticizer: 0 to 10% maximum.

These design variables were weight percent on the wet polymer. The response variables were:

- Viscosity: initial, 1 day, 3 day;
- pH;
- Rolling ball tack;
- Probe tack;
- Quick stick;
- 180° peel;
- Loop tack, and
- Holding power.

Details of the experimental are listed in Appendix 1. The actual design is as follows:

Table 1 – DOE Design Variables

Run Number	Polymer	Plasticizer	Tackifier
1	0.763	0.003	0.234
2	0.963	0.037	0.000
3	0.900	0.100	0.000
4	0.835	0.087	0.078
5	0.900	0.100	0.000
6	0.858	0.000	0.142
7	0.929	0.000	0.071
8	0.781	0.058	0.161
9	0.600	0.100	0.300
10	0.670	0.074	0.256
11	0.700	0.000	0.300
12	0.600	0.100	0.300
13	0.929	0.000	0.071
14	0.710	0.100	0.190
15	0.700	0.000	0.300
16	0.963	0.037	0.000

The DOE used was the same for both systems. In the case of the lower Tg polymer, the other ingredients in the formulation were hidden but in the case for the higher Tg polymer only the polymer, plasticizer and resin dispersion were employed in the adhesive. As stated above, it should also be pointed out again that the polymer and the resin dispersion were entered in as “wet” rather than dry ingredients into the DOE, and also note that in the mixture design the design variables were entered in as adding to one, not weight or %.

Results and Discussion

The results of the evaluation DOEs are listed in Tables 2 and 3 in Appendix 2. It is clearer to illustrate the data by reviewing the figures from the DOE experiment. The data will be discussed below by test. To make it simpler to observe the, -40°C Tg and -20°C Tg polymer data will be illustrated side by side.

The first test data are on the viscosity of the adhesives, as shown in Figures 1a and 1b.

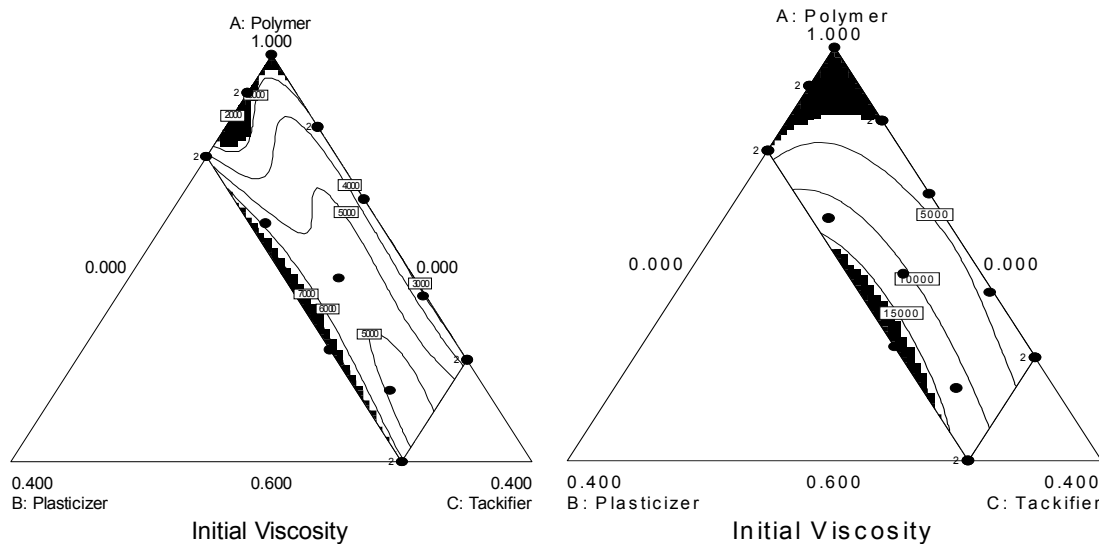


Figure 1a – Viscosity of the -40° Tg Polymer Figure 1b – Viscosity of the -20° Tg Polymer

Because of the restriction of using black and white in the presentation paper it is difficult to discern the flow of the contour maps. However, it is clear from the contours above that plasticizer does increase the viscosity of the adhesive as it is increased. In the -40°C Tg Polymer DOE, it can be suggested that the influence of the tackifier resin changes the appearance of the curves and the interaction is somewhat more complicated than is seen in the case of the -20° Tg Polymer DOE trace.

The Tgs of the formulations evaluated in the DOEs are shown in Figures 2a and 2b. As expected, the plasticizer content will depress the Tg of the adhesive but because of the resin in the system perhaps it seems to be non-linear as might have been expected. The Tg of the resin is higher than either the polymer or the plasticizer here.

The enhancement of tack is certainly a reason to add plasticizer to a PSA. Loop, rolling ball and quick stick were ways in which tack was measured. Figures 2a and 2b illustrate the loop tack data for both systems. Plasticizer in both polymer PSAs did affect tack positively. The loop tack is less sensitive to plasticizer increase in the -40°C polymer PSAs than in the higher T_g PSAs.

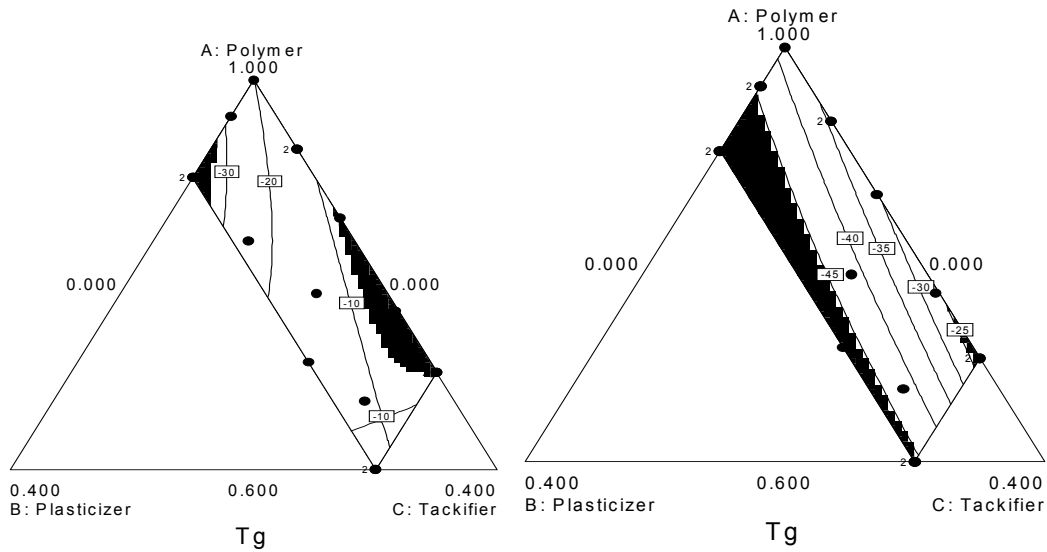


Figure 2a – T_g s of the -20°C Polymer Figure 2b T_g s of the -40°C Polymer

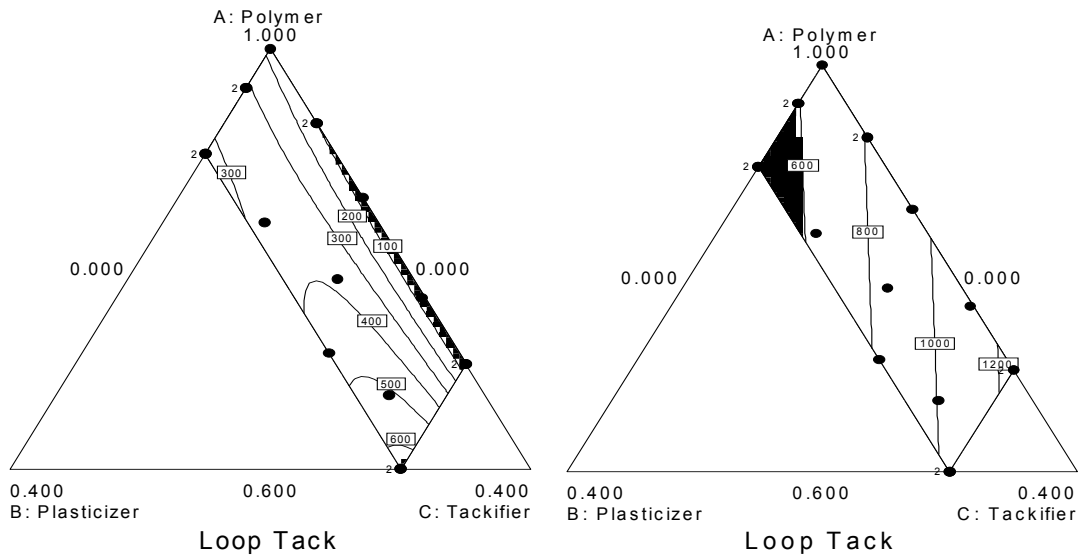


Figure 3a – Loop tack of the -20°C Polymer Figure 3b – Loop tack the -40°C Polymer

The quick stick data are in Figures 4a and 4b. The positive effect of plasticizer is seen in the -20°C PSAs. Plasticizer increase does affect the quick stick in the case of the other formula but seemingly to a less extent than in the higher temperature T_g polymer PSAs.

Rolling ball tack is illustrated in Figures 5a and 5b. In the case of the -40°C polymer PSA formulations it is clear that the plasticizer content can positively affect the tack of adhesives, whereas in the case of the -20°C polymer PSA formulations there is a very dramatic increase in tack with plasticizer addition. However, the polymer really had such poor tack by this measure in the data for low plasticizer or high tackifier levels that they could not be measured. DOEs don't like discontinuities like that so when the test exceeded the maximum length of tape tested, the data point value was set to that length (30 cm).

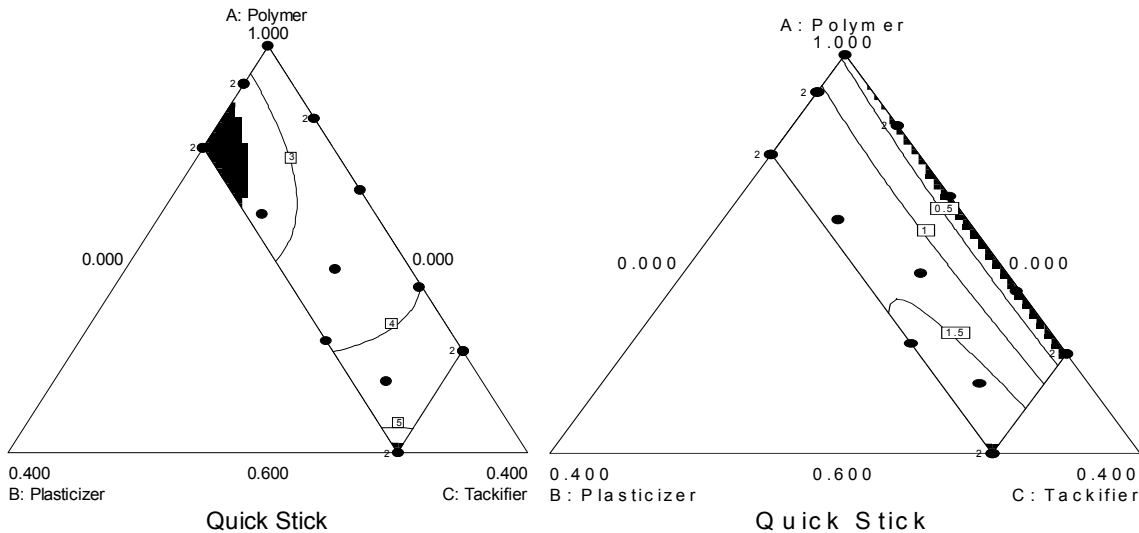


Figure 4a – Quick Stick for the -40°C Polymer Figure 4b – Quick Stick for the -20°C Polymer

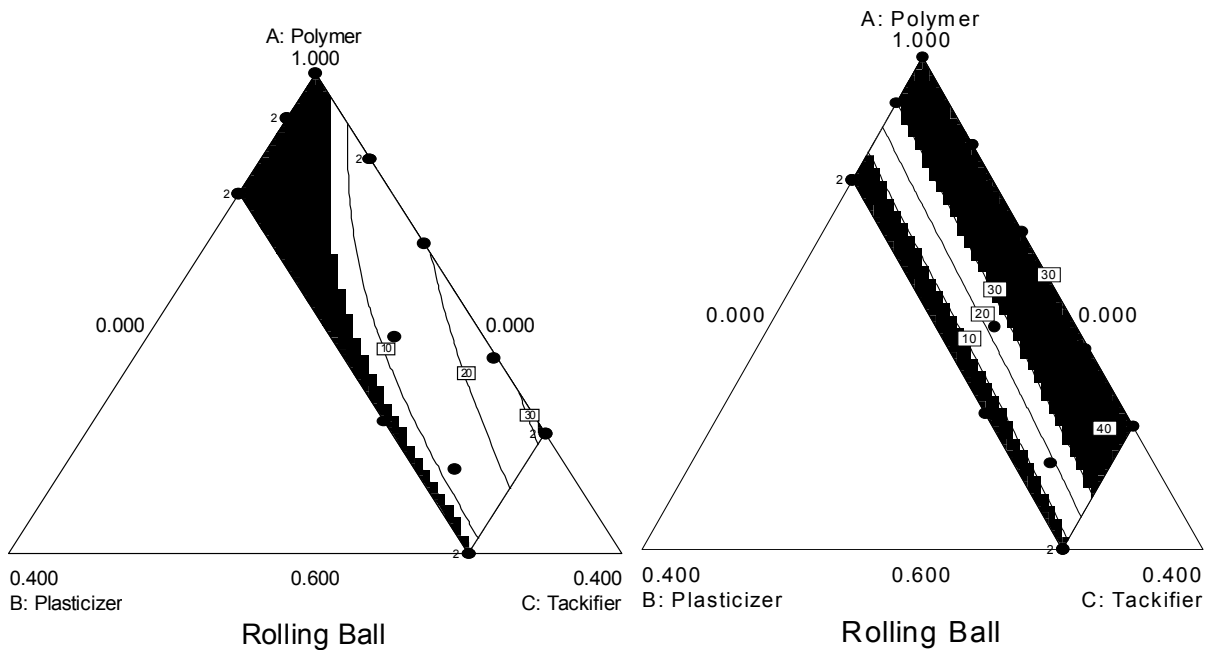


Figure 5a – Rolling Ball Tack for the -40°C Polymer Figure 5b – Rolling Ball Tack for the -20°C Polymer

The next parameter is probe tack, which is yet another way to look at the tack of a PSA. Figures 6a and 6b show this data. In both sets of data the plasticizer significantly increases the probe tack of the PSA's evaluated. In particular, the tack of the -20°C polymer PSAs significantly increased with more plasticizer in the formulation.

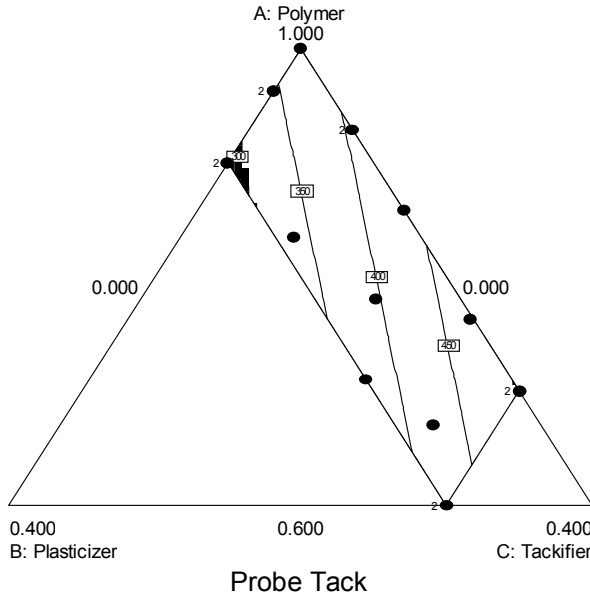


Figure 6a – Probe Tack of the -40°C Polymer

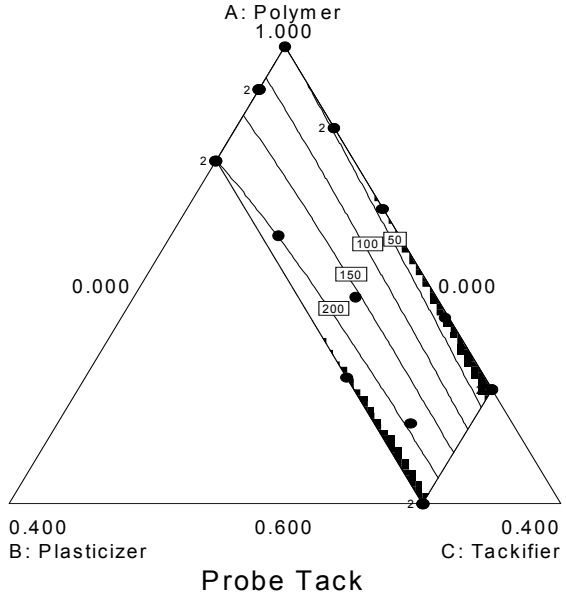


Figure 6b - Probe Tack of the -20°C Polymer

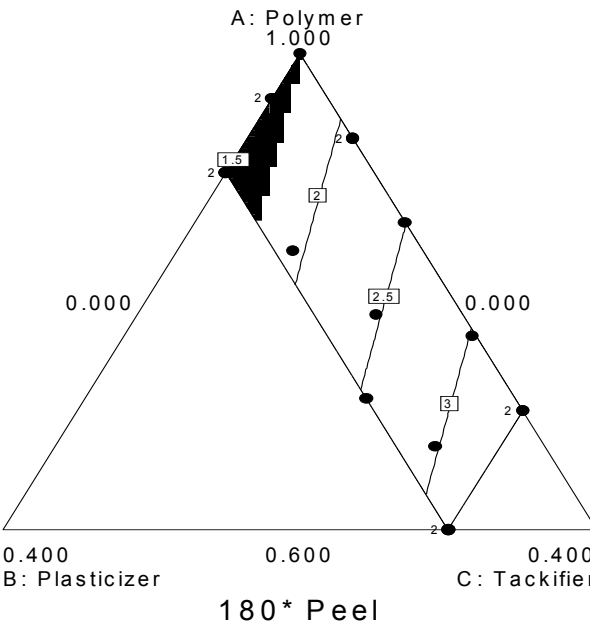


Figure 7a - 180° Peel of the -40°C Polymer

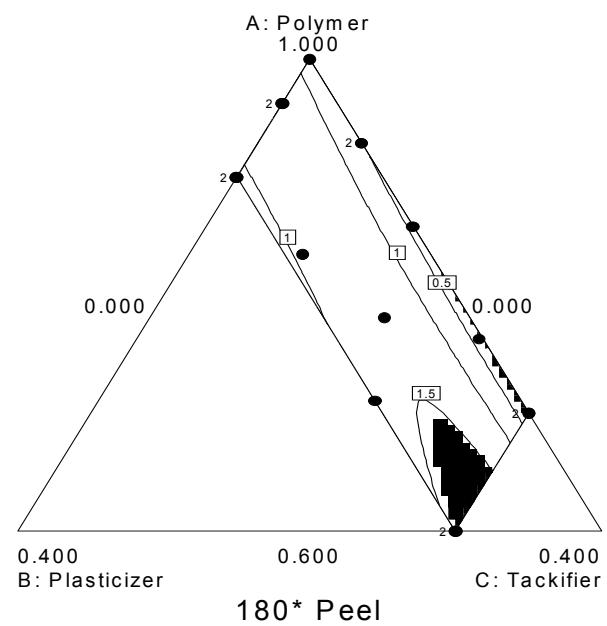


Figure 7b - 180° Peel of the -20°C Polymer

The 180° peel data are illustrated in Figures 7a and 7b. In this case the plasticizer content does not have a large effect on the peel strength. It appears that the polymer and resin content seem to have stronger influences than the level of plasticizer used.

The holding power data is clearly strongly influenced by the level of plasticizer or (to a lesser extent) tackifier used in the formulation. Figure 8a and 8b clearly show this. As might be expected, the lower Tg polymer PSA adhesives did not have high holding power, certainly not as much as the higher Tg polymer PSAs.

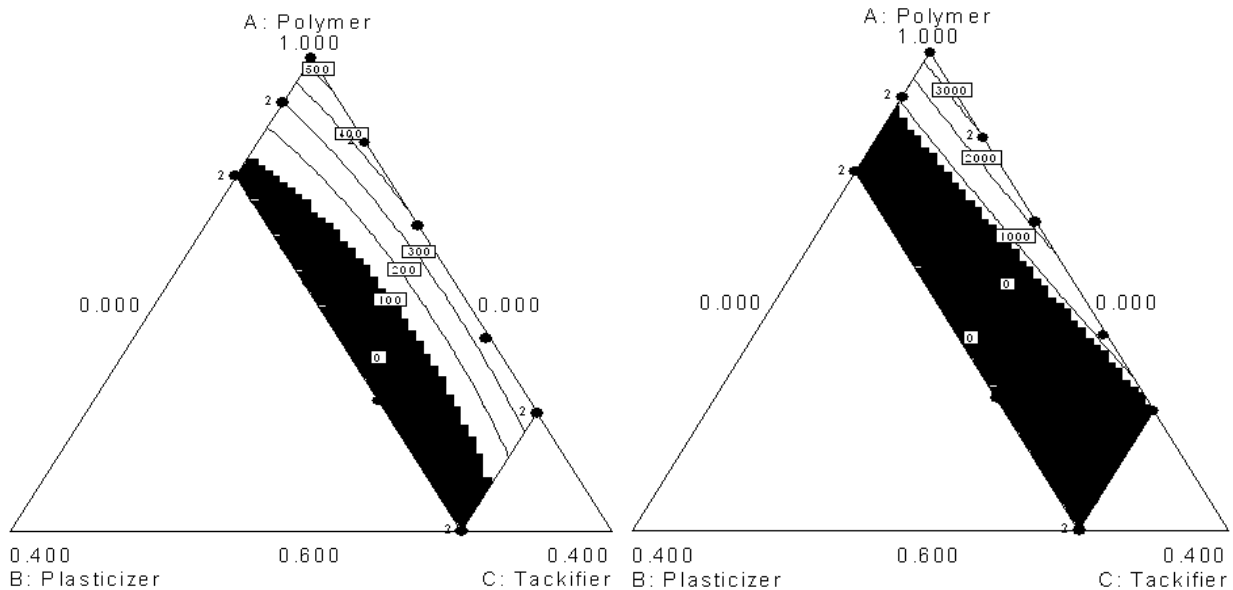


Figure 8a – Shear (Holding Power) for the -40°C Polymer Figure 8b Shear (Holding Power) for the -20°C Polymer

Conclusions

Plasticizer addition will definitely affect the performance of a waterborne PSA. It was specifically observed that a dibenzoate plasticizer blend will:

- Change the glass transition temperature of the PSA. This change indicates that the plasticizer is compatible in the systems tested and also is a precursor to the other effects to be considered.
- Have an effect on the viscosity of the adhesive. In this case, the effect was an increase and this is also an indicator of compatibility of a plasticizer in a waterborne adhesive. This is also a factor on the solids of the adhesive being considered.
- Increase tack – All of the measurements of tack that were employed showed that a plasticizer used in a PSA will affect the tack characteristics of the PSA. The type of polymer used, as well as the resin content, certainly will also dictate the magnitude of this effect or type of effect. The issue is an equilibrium of the use of tackifier and balance of

performance required. The plasticizer will allow use of less tackifier, if so desired, and may also moderate the resin's effects. This was noted earlier in the references cited.

- Diminish the holding power of the adhesive. As is the case in all formulation design, what is required for this parameter for the application is the critical question. These data may indicate that a higher Tg polymer with a higher molecular weight polymer may best benefit from the use of a plasticizer if the tack is low.
- Affect 180° peel. The parameter least affected by plasticizer content seemed to be 180° peel. It was affected by plasticizer content, but not as strongly as at first may be suspected.

It should also be pointed out that one dibenzoate blend (a blend of diethylene glycol, dipropylene and propylene glycol dibenzoate) was used in these experiments. Dibenzoates in general are compatible with acrylic polymers as well as the resins used to formulate waterborne PSA's and it would be expected that most of the dibenzoate family would be applicable to this application. The DOE data generated also indicates that it is possible to use this tool to help formulation.

Appendix 1

Experimental

Preparation: The adhesives were prepared by mixing the plasticizer and resin dispersion into the polymer for 10 minutes at 750 RPMs using a Caframo outfitted with a Jiffy blade. The plasticizer was added within the first minute of mixing and the resin shortly thereafter. Tapes were prepared on 1 or 2 mil polyester films with a 1 mil adhesive film thickness.

Viscosity: The viscosity response of the emulsions to the plasticizers were determined at low shear by a 30 second reading at 20 RPMs on a Brookfield DVII, RV viscometer (22°C ± 2°C) after initial (one hour), 1 day and 3 days. (ASTM D-1823 reference)

Glass Transition: The glass transition data was gathered on 10 mg samples of 10 mil wet film that had dried at least overnight. Samples were run by jumping from room temperature to -90°C and then ramped at 10°C per minute on a TA Instruments Q2000 DSC.

pH – ASTM E-70

Rolling ball tack – ASTM D-3121: Trough and specimen were placed on a large glass plate. Trough was cleaned with acetone three times and allowed to dry for 10 minutes. Specimen was arranged adhesive side up in line with the trough. Prior to each roll of the ball, the ball was cleaned with acetone three times and allowed to equilibrate to room temperature. Clean, dry tongs were used to place the ball at the top of the trough. The ball was then released and allowed to roll to a stop on the specimen. The distance from the point where the ball initially contacted the adhesive to where the ball stopped was measured.

Probe tack – ASTM D-2979: The tack tester probe was cleaned with acetone and a Kimwipe, then wiped dry. The specimen was applied to the annular ring weight, which was then placed in the carrier. At a speed of 10 mm/s, the probe was brought into contact with the specimen for one second, then separated from the specimen at a speed of 10 mm/s. The tack was recorded as the max force required to separate the probe from the adhesive (in Newtons)

Quick stick – PSTC – 5: Specimen was draped onto stainless steel test panel as outlined in the PSTC method. The panel was immediately inserted into a 90° peel fixture and pulled at 12"/min. The average peel value obtained between 1" and 3" was reported.

180° peel – PSTC – 101: 12 mm of tape was folded at one end to form a tab. The other end of the specimen was touched to one end of the test panel, then rolled mechanically twice in each lengthwise direction, preventing air from being entrapped below the tape. Specimens were tested within one minute of preparation. The folded end of the tape was doubled back at an angle of 180° and pulled using the rate of 5 mm/s. The average peel strength from between 24 and 72 mm was reported.

Loop tack - PSTC 16: A 5" x 1" loop of tape was affixed to the top grip of the tensile tester, set with a distance of 1" from the bottom plate. The tensile tester brought the bottom steel plate up at a rate of 12"/min until the loop of tape wetted out 1 in² of the steel plate, then reversed direction and pulled the plate away at a speed of 12"/min. The average peak force was reported in gf.

Holding power – PSTC 107-A: The test specimen was centered one end of a steel panel and applied without added pressure to cover an area exactly 12 x 12 mm. The applied test area was rolled down twice in each lengthwise direction using the 5 lb roller. Within one minute, the test assembly was placed in the test stand so that the free end was vertical and hung with a weight (500 g for the -40°C Tg Polymer, 1000 g for the -20°C Tg Polymer). The time elapsed until the specimen had completely separated from the test panel was recorded.

Appendix 2

Table 2a – Lower Tg Polymer PSA DOE Test Results

Run	Initial	1 Day	3 Day	pH
	<i>Viscosity, mPa.s</i>	<i>Viscosity, mPa.s</i>	<i>Viscosity, mPa.s</i>	
1	3124	3030	3050	5.4
2	2104	2110	2120	5.0
3	4240	4150	4330	5.2
4	5610	5510	5580	5.2
5	4640	4540	4490	5.3
6	3300	3340	3370	5.3
7	3130	3090	3120	5.3
8	5200	5240	5260	5.3
9	6160	6410	6380	5.3
10	4840	5130	5060	5.3
11	3340	3070	2740	5.3
12	6160	6280	6150	5.3
13	3070	2860	2790	5.3
14	7670	7890	8170	5.3
15	3160	2790	2580	5.3
16	2920	2630	2630	5.3

Table 2b – Lower Tg Polymer PSA DOE Test Results

Run	Shear Adhesion (500 g, min)	Rolling Ball (cm)	Probe Tack (g)	180° Peel Strength (psi)	Quick Stick Peel Strength (psi)	Loop Tack (gf)
	<i>Avg</i>	<i>Avg</i>	<i>Avg</i>	<i>Avg</i>	<i>Avg</i>	<i>Avg</i>
1	310	34.0	474.7	2.60	3.07	1357
2	226	6.0	302.8	1.56	2.39	569
3	56	5.2	263.6	1.32	1.95	504
4	51	7.6	321.3	1.54	2.51	568
5	56	3.2	313.8	1.42	2.28	447
6	344	14.5	357.6	2.33	3.99	746
7	453	11.6	507.9	2.41	3.72	833
8	73	11.2	353.6	2.08	3.65	756
9	22	8.7	427.1	3.02	5.08	1031
10	41	9.0	488.2	3.58	4.47	994
11	362	31.1	442.6	2.93	4.88	1038
12	22	6.6	451.7	3.36	5.62	1182
13	459	13.2	391.3	2.01	3.53	678
14	33	8.5	335.0	2.73	3.85	762
15	489	29.6	525.0	3.83	4.32	1359
16	376	4.7	369.5	1.93	3.15	603

Table 3a – Higher Tg Polymer PSA DOE Test Results

Run	Initial	1 – Day	3 – Day	pH
	<i>Viscosity, mPa.s</i>	<i>Viscosity, mPa.s</i>	<i>Viscosity, mPa.s</i>	
1	5620	4320	3680	5.0
2	752	748	728	4.7
3	3490	3410	3530	4.7
4	12800	12820	12720	4.8
5	3100	3280	3240	4.6
6	4120	3900	3950	4.8
7	2590	2720	2740	4.7
8	10520	10400	9620	4.8
9	13000	12700	11680	4.9
10	12280	11000	10640	4.8
11	2810	2700	2590	5.0
12	13700	13700	12160	5.0
13	3000	3140	3240	4.9
14	18300	17700	17000	5.0
15	2750	2590	2600	5.1
16	692	704	704	4.9

Table 3b – Higher Tg Polymer PSA DOE Test Results

Run	Shear Adhesion (1000 g, min)	Rolling Ball (cm)	Probe Tack (g)	180° Peel Strength (N/cm)	QS Peel Strength (N/cm)	Loop Tack (gf)
	Average	Average	Average	Average	Average	Average
1	544	>30	30	0.44	0.26	102
2	376	>30	93	2.04	1.38	213
3	65	4.9	199	1.42	2.10	266
4	82	7.4	212	1.85	0.27	367
5	71	6.3	200	1.40	1.42	206
6	1424	>38	50	0.61	1.25	56
7	2714	>40	28	0.96	1.48	96
8	153	23.1	157	2.59	1.15	317
9	22	6.7	233	2.68	0.19	698
10	69	18.5	194	2.97	1.37	494
11	779	>33	6	0.29	0.11	22
12	22	7.8	263	2.85	1.92	588
13	4060	>28	43	1.02	0.28	108
14	21	6.1	226	1.95	1.51	480
15	1143	>42	9	0.37	0.13	35
16	1058	> 42	132	2.41	0.86	476

References

1. Arendt, William D. "ASC Additives Short Course: Plasticizers", November 7, 2007.
2. Satas, Donatas, *Handbook of Pressure-Sensitive Adhesive Technology*, Van Nostrand Reinhold Co. New York, NY 1982, Page 325.
3. Satas, Donatas, *Handbook of Pressure-Sensitive Adhesive Technology, Second Edition*, Van Nostrand Reinhold Co. New York, NY 1989, Pages 431, 470 to 472.
4. Satas, Donatas, *Handbook of Pressure-Sensitive Adhesive Technology*, Van Nostrand Reinhold Co. New York, NY 1982, Pages 290 to 296.
5. Satas, Donatas, *Handbook of Pressure-Sensitive Adhesive Technology, Second Edition*, Van Nostrand Reinhold Co. New York, NY 1989, Pages 329 to 331.
6. Horst, Roland H., "Rheological Analysis for Development and Quality Assurance of Pressure Sensitive Adhesives" PSTC Tape Summit 35, 2012.
7. Petrie, Edward M. "Fundamentals of Pressure Sensitive Adhesives Part I – Types and Formulation", Specialty Chemical presentation, September 5, 2012.
8. Chang, E. P., "Viscoelastic Windows of Pressure-Sensitive Adhesives", *The Journal of Adhesion*, 34: 1, 189 — 200 (1991)
9. Satas, Don, "Correlation of Pressure Sensitive Adhesive Performance With Its' Rheological Properties", TAPPI Proceedings, 1989 Polymer Laminations and Coatings Conference, September 5-8, 1989, Pages 699-703.
10. Tsaur, Tom, "The Effect of Mineral Oil on Hot Melt Pressure Sensitive Adhesives", PSTC TECH 32 Technical Seminar, Pages 59 to 70, 2009.
11. Arendt, William D., "Plasticizers in Hot Melt Adhesives", Adhesive and Sealant Councils Hot Melt Short Course, 2011.
12. Tkaczuk, Peter, "Statistical Experimental Design in the Development of Pressure Sensitive Adhesives", TAPPI Proceedings, 1989 Polymer Laminations and Coatings Conference, September 5-8, 1989, Pages 705-720.

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