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HIGH EFFICIENCY POLYMERS FOR HOT MELT PRESSURE SENSITIVE ADHESIVES

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Paul Dalley graduated from Hope College in 1985 with a B.S. in Chemistry; obtained a Masters in Polymer Chemistry from the University of Detroit-Mercy in 1992; and in 2006 Paul obtained a J.D. from Marquette University Law School. Paul holds licenses for the State of Wisconsin, and the United States Patent and Trademark Office. Paul has over fifteen years of experience in formulating hot melt adhesives for product assembly applications. Prior to law school, Paul worked for such notable adhesive companies such as, Dow Automotive, Bostik, and H.B. Fuller. Paul joined Dexco Polymers in August, 2012.

HIGH EFFICIENCY STYRENE ISOPRENE STYRENE BLOCK CO-POLYMERS FOR HOT MELT ADHESIVES

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Introduction

There are many challenges facing today's hot melt formulator. Pressure to reduce costs and variations in availability of raw material supply often challenges the formulator. Fortunately, high efficiency styrene isoprene styrene (SIS) polymers are available to help today's formulator meet these challenges. High efficiency polymers help the formulator to reduce formulation viscosity or increase formulation flexibility by allowing the exchange of resin or oil for polymer.

Lower viscosity formulations provide numerous advantages, such as lower application temperatures. Lower application temperature minimizes warping of heat sensitive substrates. This may allow for the use of thinner substrates providing a cost savings to the end user. They are easier to spray, which allows for faster line speeds and thinner application lines. Lower application temperature lengthens pot life and improves safety for the production operators.

Improved formulation flexibility allows the formulator to exchange resin or oil for polymer. Exchanging oil for polymer reduces formulated cost. While exchanging resin for polymer, in addition to reducing formulated cost, allows the formulator to manage supply variation.

There are two approaches used to develop high efficiency SIS block co-polymers. The first being polymer structure, and the second being polymer molecular weight. In terms of polymer structure, radial polymers are more efficient than the linear polymers in that they can duplicate adhesive performance at a lower viscosity and or lower polymer loading levels. On the other hand, a higher molecular weight linear polymer can be further extended with oil or resin compared to their radial or lower molecular weight linear counter parts. This article will illustrate the use of these two types of polymers in hot melt PSA formulae. The physical properties of the polymers referenced in this article are listed in Table I.

Table I. Polymer Properties

Polymer	Structure	Styrene, Wt. %	Melt Flow Rate, dg/min	Diblock, Wt. %
A	Linear	18	12	<1
B	Linear	15	10	18
C	Radial	20	14	30
D	Radial	21	7	22
E	Linear	32	<3	<1

Experimental

All the formulae discussed in this article were prepared in solution at 50% wt. /wt. solids in toluene. The formulae were then cast as a 1.5 mil film on 2 mil Mylar. The remaining liquor was devolatilized *in vacuo* to produce a solid mass. The film samples were tested to stainless steel for shear adhesion failure

temperature (SAFT), 180 degree peel, loop tack and rolling ball tack. The devolatilized samples were used to measure melt viscosity. The test methods used in this article are detailed in Table II.

Table II. Adhesive Test Methods

SAFT (Shear Adhesion Failure Temperature)	To stainless steel; units = °C	PSTC-107
180 degree peel	To stainless steel at ASTM conditions; units = lbs/in	ASTM D33330M; PSTC-101
Loop Tack (LT)	To stainless steel at ASTM conditions; units = lbsF	PSTC-16
Rolling Ball Tack (RBT)	Units = cm; 24 cm maximum	PSTC-6
Adhesive Viscosity	Brookfield viscometer at specified temperature, units = cP	ASTM D3236-04

Radial SIS Block Co-polymer D

Polymer D is a four armed radial SIS based polymer. Polymer D was solution blended into a typical packaging tape formulation using: a midblock resin, naphthenic oil, and a hindered phenol antioxidant. For comparison, the same formula was made using polymer B, a linear SIS based polymer. The test results for each formulation are listed in Table III.

Table III. Polymer B – Control v. Radial Polymer D, Wt. %

Status	Run No.	Polymer		Resin	Oil	AO	Visc. @ 177° C	SAFT	180° Peel
		B	D						
Control	1	39.7	0.0	55.5	4.0	0.8	75,000	73.0	6.4
Offset	2	0.0	39.7	55.5	4.0	0.8	20800	79.3	1.6
Optimized	3	0.0	36.6	53.6	9.0	0.8	15,000	73.1	5.6

In the same formulation, the radial polymer has a much lower viscosity than the linear polymer. Run Number 2, Table III, using polymer D has a melt viscosity of 20,800 cP. In comparison, Run Number 1, Table III, using polymer B has a melt viscosity of 75,000 cP at the same temperature. So as a direct replacement for the linear polymer, the radial gives a better than threefold reduction in viscosity compared to the standard formulation.

Radial polymers, however, cannot be used as a mere drop in for linear polymers. When polymer B was replaced one for one with polymer D, there was a significant drop in peel, 1.8 lbs/in compared to 6.4 lbs/in. So, additional formulating is required to approximate the base formula. For Run Number 3, Table III, minor adjustments were to the polymer, resin and oil. The resulting adhesive matches the SAFT of the linear formula and closely approximates the peel value. Moreover, there is a further reduction in the viscosity from 20,800 cP to 15,000 cP at 177° C, a considerable drop from the 75,000 cP of the base formula. So with proper formulation, a radial polymer can be used to produce adhesives with lower melt viscosity than their linear counter parts.

Additionally, radial polymers can be extended and still produce useful hot melt PSAs. Figure 1, describes the effect of reduction of polymer content on viscosity, SAFT, 180 degree peel, loop tack, and

rolling ball tack. For this data set, the concentration of polymer was reduced while maintaining the same resin to oil ratio. In this case radial polymers D and C are compared to the linear, nearly 100% tri-block polymer, A.

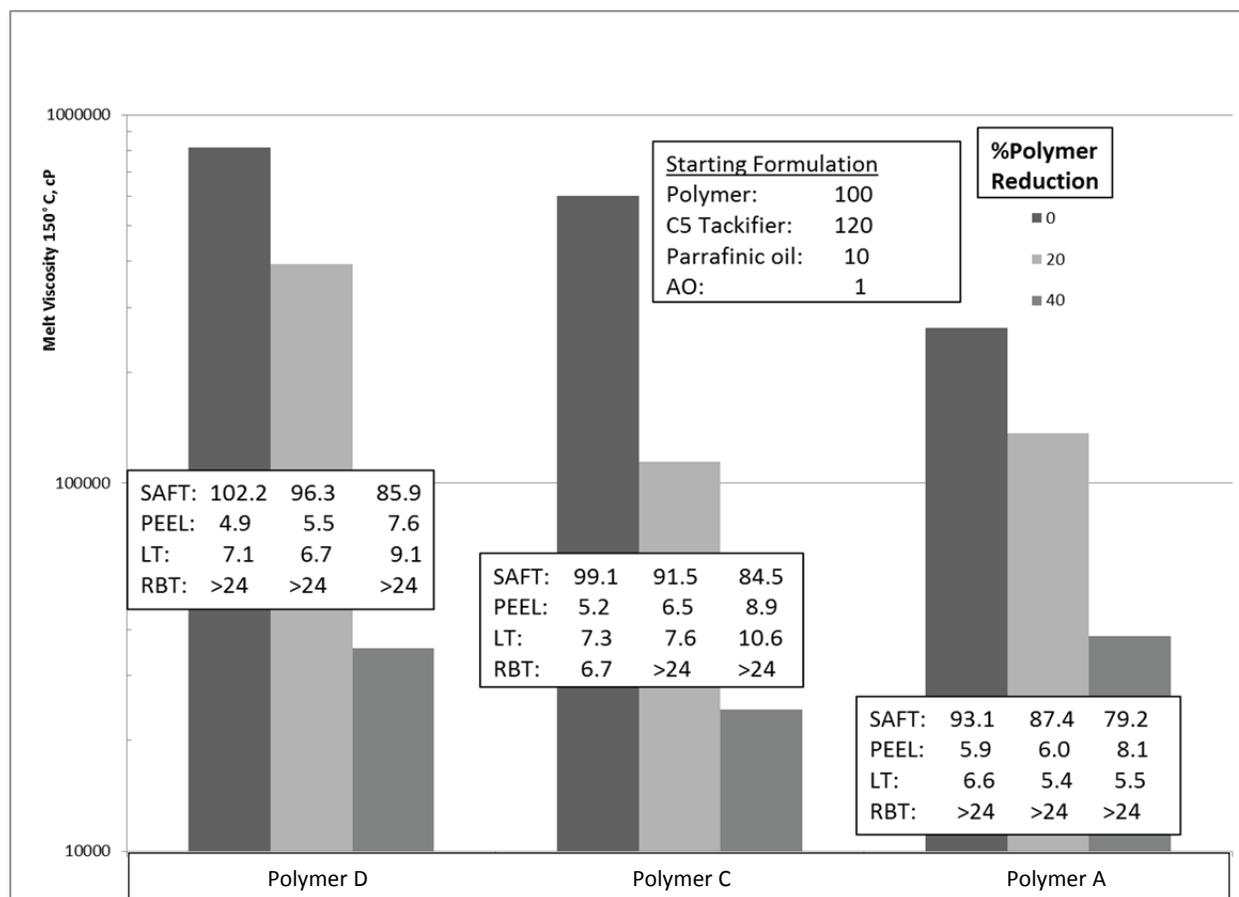


Figure 1. Reduction in Polymer Content

For each step reduction in polymer, the radial polymers had a larger relative drop in viscosity than the linear polymer. Additionally, the radial polymers had better SAFT retention than the linear polymers. Both radial polymers maintained SAFTs above 80° C despite a 40% reduction in polymer content.

For all the polymers, peel increased as the polymer content decreased. However, the effect on tack is not quite as clear. For the radial polymers loop tack increased when the polymer was reduced by 40%, but the response was more flat for the linear polymer. For polymer C, rolling ball tack increased as the polymer decreased, but remained unaffected for the polymer D and A runs. The data indicates that radial polymers can be extended to manage cost or raw material supply while maintaining adhesive properties.

A formula may also be extended by simply increasing the oil content. In this way, both cost and viscosity are reduced. Figure 2, describes effect of increasing oil content on viscosity, SAFT, 180 degree peel, loop tack, and rolling ball tack. Generally, the radial polymers, D and C show a greater reduction in viscosity than the linear polymers A and B. Additionally, radial polymers maintained better shear values as the amount of oil is increased compared to the linear polymers.

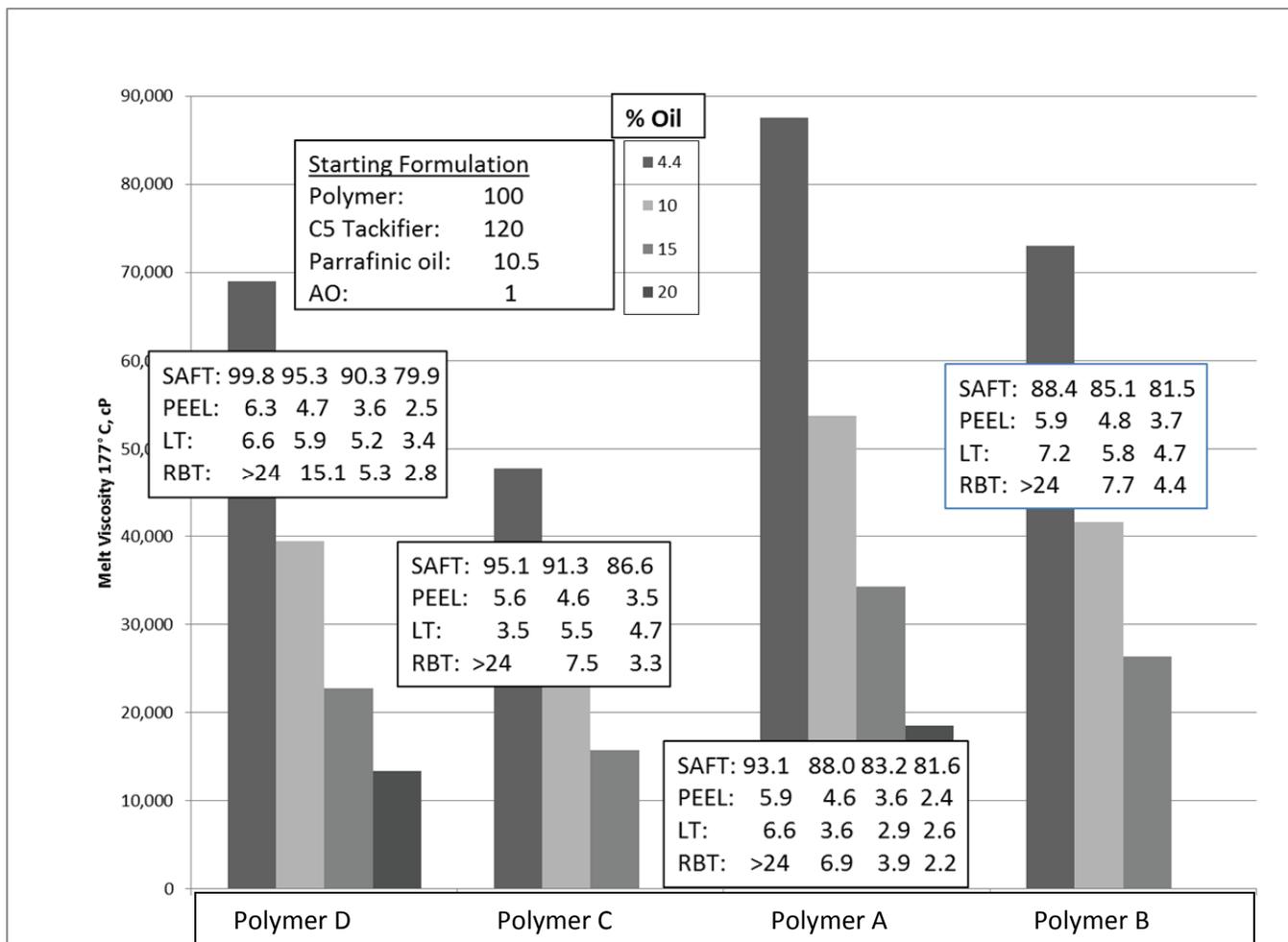


Figure 2. Increase in Oil Content

In all cases, the peel values decrease as the oil content is increased. Similarly, both loop tack and rolling ball tack decrease as the percent oil increases. Baring in mind, however, that for rolling ball tack, a decrease is a positive. A shorter rolling distance indicates a tackier adhesive.

Comparing the results described in Figures 1 and 2, it is clear that a formulated extension of polymer yields a more functional adhesive rather than mere dilution with oil. Nonetheless, radial polymers can be extended while maintaining useful adhesive properties compared to linear polymers. With minimal reformulation, it is possible to replicate the desired properties of formulae made with linear polymers while achieving a lower overall viscosity. Thus, radial polymers are useful to the adhesive formulator.

High Molecular Weight Linear Polymers

Although a radial structure does have utility, a high molecular weight linear polymer can be significantly extended while maintaining properties of the base formula using lower molecular weight linear polymer. Table IV, lists a comparison of polymer B formulated in a packaging tape formulation, compared to a variety of formulae using an experimental high molecular weight SIS polymer E. The design objectives of each run were to: (1) meet or exceed the SAFT of the polymer B formula; (2) have a peel strength of

greater than 3.5 lbs/in; and (3) maintain a loop tack close to that of the base formula. The test results, Runs 1-9, in Table IV are forced ranked by polymer concentration.

Table IV. Hot Melt Adhesives Based on High Molecular Weight SIS, Wt. %

Run No.	Polymer	Resin	Oil	A.O	SAFT	180 Peel	Loop Tack
Poly. B	39.7	55.5	4.0	0.8	73.0	6.4	2.3
1	37.7	49.7	12.7	0.5	95.7	6.3	1.9
2	33.3	45.3	21.3	0.5	90.4	6.5	3.0
3	29.0	54.0	17.0	0.5	90.0	8.8	2.5
4	29.0	41.0	30.0	0.5	79.3	4.3	4.7
5	27.2	43.9	28.4	0.5	82.3	4.4	5.0
6	27.0	52.6	19.9	0.5	86.7	8.2	3.7
7	25.0	45.6	28.9	0.5	78.9	6.0	6.0
8	24.7	49.7	25.7	0.5	76.8	7.0	4.7
9	22.0	52.7	24.8	0.5	74.9	7.2	8.0

Runs 1-9, Table IV, show clear trend of decreasing SAFT with polymer concentration. Run number 1 with 37% polymer has a SAFT of 95.7 C; where run number 9 with 22.0% polymer has an SAFT of 74.9 C. Peel and Loop Tack, however, do not show a clear trend with respect polymer concentration. This is not a concern rather it indicates formulation flexibility.

The data in Table IV indicates that, using the exact same set of raw materials that objectives 1-3 can be met using a variety of formulae. By simply re-apportioning the levels of polymer resin and oil the design objectives can be met. Moreover, Runs 1-3 and 6-9 either meet or exceed all the properties of the base formula. Essentially providing six different ways to meet or exceed properties of the base formula. Such flexibility helps the formulator to balance adhesive performance against raw material supply.

The results in Table IV indicate that all the formulae meet the above requirements using a lower concentration of polymer than the base formula using polymer B. Moreover, all the formulae use considerably more oil than the base formula. Thus, Runs 1-9, Table IV, have a lower formulated cost than the base formula.

The runs provided Table IV, were abstracted from broader simplex centroid mixture design.^{1,2} The details of the full design are summarized in Appendix A. Appendix A provides the full set of runs and the test results. It also lists Figures 3 – 5, which are contour maps that more fully describe the relationships between the raw materials and the adhesive properties listed in Table IV.

Summary

High efficiency SIS block co-polymers offer many advantages to the hot melt formulator. Radial polymers produce useful adhesives at a lower viscosity and can be extended to reduce cost. Similarly, a higher molecular weight polymer can be further extended allowing for additional formulation flexibility and reduction in formulated cost.

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APPENDIX A – MIXTURE DESIGNS

Simplex Centroid Mixture Designs

Simplex mixture designs are a subset of response surface designs. These designs differ from other designs in that all the components must total to one (1). A classic centroid design is best thought of as an equal lateral triangle with the maximum value for each ingredient at the vertex, and the minimum value plotted in the center of the opposing edge, and a center point with equal proportions of the ingredients. These points are listed in Table V as Vertex, Center Edge, and Center. Classically, the vertices have a value of 1, the center edges have a value of 0, and the center is a 1/3, 1/3, 1/3 blend of each ingredient.

Adhesive blends rarely fit the classic model. Thus, the design is “constrained” while maintaining requirement of all the components must total to one. A constrained design differs from the classic design in that it is “flipped.” That is, the minimum values are located at the vertices, while the maximum values are located at the center edges. Illustrated in Figure 3, the minimum value for the polymer is located at the top of the triangle at, 16%, while the maximum value of 42% is located at the center edge opposite.

Furthermore, the design listed in Table V, is an “augmented” design. Augmenting the design involves adding replicate runs, and axial blends. Axial blends are listed as Axial Points in Table V. Lastly, each of the points described in Table V are illustrated in Figures 3 – 5. Figure 3 is reproduced twice. The first iteration lists points discussed, and further describes other elements of a contour diagram. The second is a clean copy of Figure 3. The results of the design are summarized in Table V, and Figures 3 – 5.

Table V. Simplex Centroid Mixture Design, Wt.%

Run No.	Point Type	Polymer	Resin	Oil	SAFT	Peel	Loop tack
1	Vertex	42.0	54.0	4.0	99.1	3.0	0.3
2	Vertex	16.0	54.0	30.0	67.5	5.0	6.2
3	Center	33.3	45.3	21.3	90.4	6.5	3.0
4	Axial	37.7	49.7	12.7	95.7	6.3	1.9
5	Center Edge	29.0	41.0	30.0	79.3	4.3	4.7
6	Vertex	42.0	54.0	4.0	100.5	0.6	0.1
7	Center Edge	29.0	54.0	17.0	90.0	8.8	2.5
8	Axial	24.7	49.7	25.7	76.8	7.0	4.7
9	Vertex	16.0	54.0	30.0	65.6	4.9	5.0
10	Axial	37.7	36.7	25.7	97.1	3.7	2.5
11	Vertex	42.0	28.0	30.0	96.6	2.6	2.5
12	Vertex	42.0	28.0	30.0	93.0	2.4	2.2
13	Center Edge	42.0	41.0	17.0	99.5	4.9	3.7
14	Center Edge	29.0	41.0	30.0	75.3	4.0	4.7

Note: 0.5% anti-oxidant was added to each of the runs.

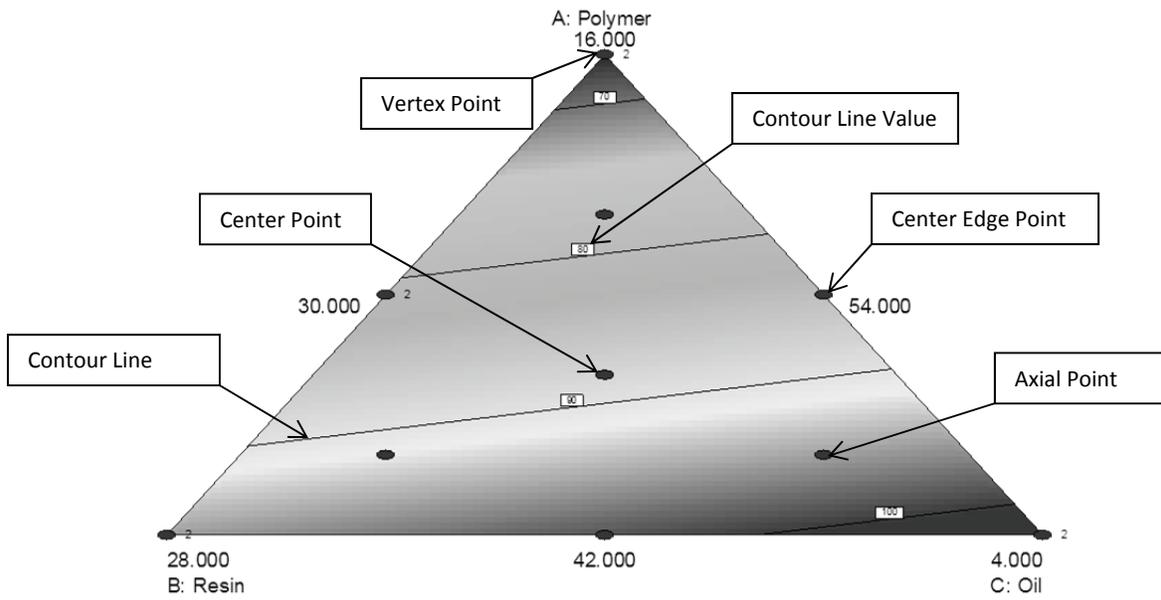


Figure 3. SAFT, C

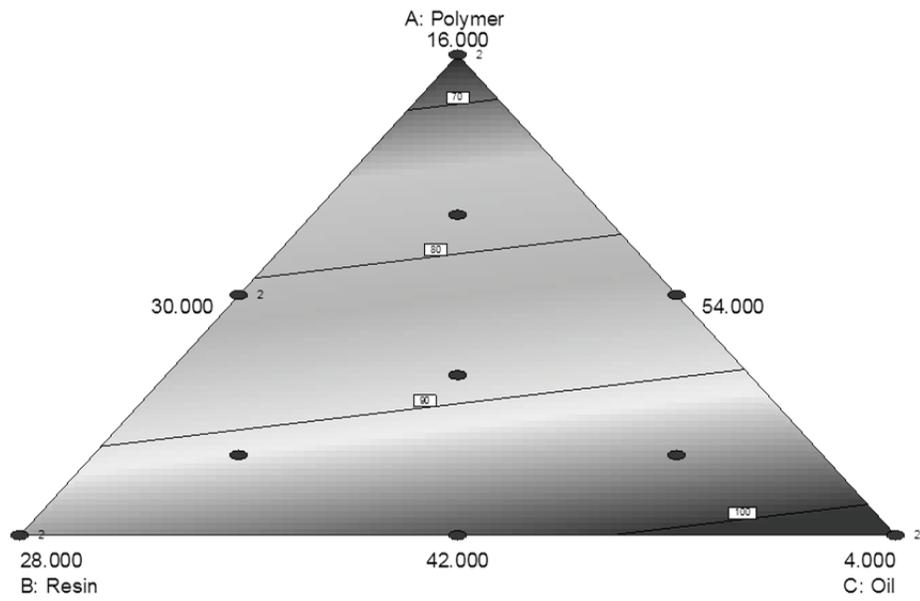


Figure 3. SAFT, C

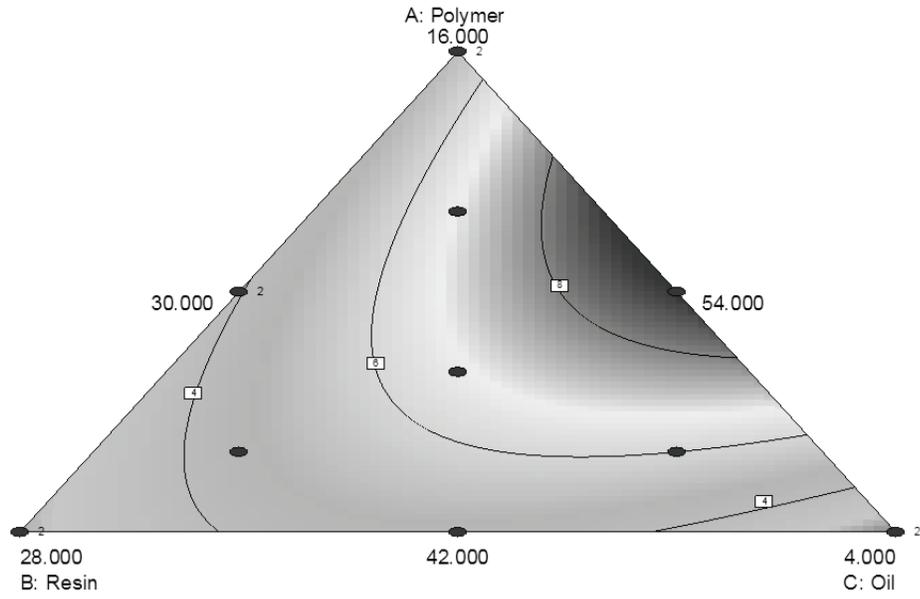


Figure 4. 180 Degree Peel, lbs/in

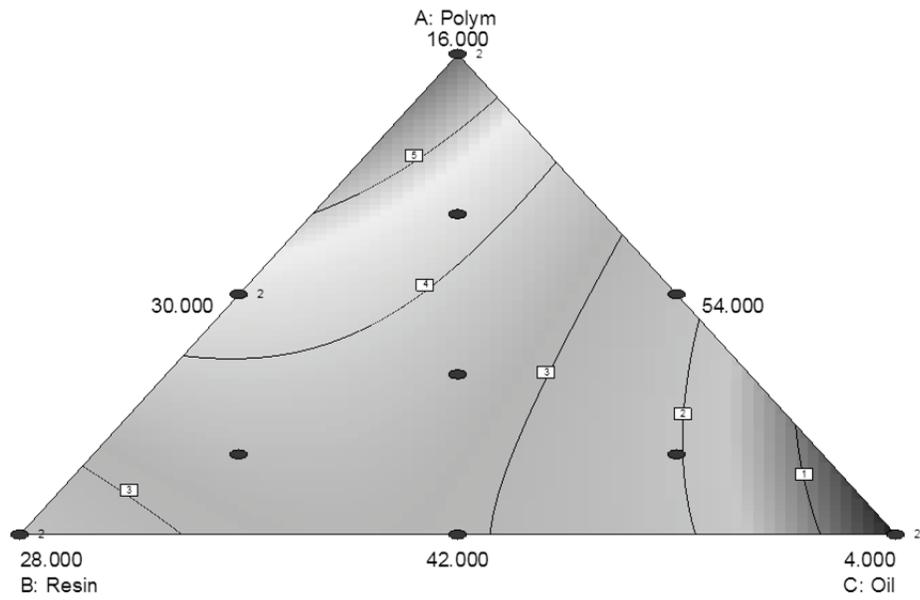


Figure 5. Loop Tack, lbF

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