

BIO-BASED TACKIFIERS FOR BOOSTING ACRYLIC PSA PERFORMANCE

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For decades, acrylic based polymers have found broad utility in pressure sensitive tapes and labels, as well as graphic films and reflective decals. The aesthetic qualities of these systems make acrylic polymers well suited for many consumer goods where appearance is valued and highly desirable. Filmic labeling exploits the attributes of a clear, water-white acrylic adhesive layer that enhances a product's presentation and eye appeal at the consumer level. By blending vivid labeling with the ability to see the actual product in a clear container, it improves merchandising as well as the perception of product quality. The beverage industry, for example, has mastered the use of clear, pressure sensitive filmic labels to enhance the appeal of their products from a health and nutrition perspective, as well as uniquely and distinctively advertise a product as simple as bottled water.

Industrial applications for acrylic based pressure sensitive adhesives utilize the inherent attributes of oxidative stability and UV resistance in many demanding applications where extended service life is an expected criterion. The ability of the adhesive to resist UV bombardment in an exterior application while maintaining its original adhesive properties at elevated temperatures for prolonged periods of time can readily be satisfied when using an acrylic PSA in many real-world scenarios. Warranted products with durability requirements found in the automotive and electronic industries rely on the versatility of acrylic based pressure sensitive adhesives to deliver and meet the needed requirements.

Co-polymerization of various acrylic and acrylate monomers under various conditions and ratios significantly expands the performance window achievable with acrylic based pressure sensitive adhesives. The glass transition temperature of these polymers can be radically manipulated to formulate freezer grade label adhesives or high temperature industrial tapes. The formulating permutations are endless when mixing and blending various reactive acrylic monomers, but there are performance voids where acrylic based pressure sensitive adhesives fall short of delivering and meeting requirements in a variety of adhesive applications and markets.

Both UV and EB curable acrylic PSAs have evolved and grown due to ever increasing performance demands. These technologies have expanded rapidly and are now practiced globally to bridge some of the technical and performance limitations. However, even these sophisticated approaches cannot provide suitable formulary options for all applications.

Solution, water-based and hot melt acrylic polymer systems can be modified with the addition of tackifying resins exhibiting the appropriate functionality and compatibility. These technologies have been extensively practiced on a commercial scale to enhance the performance of an acrylic PSA beyond traditional non-compounded limits. Tackifying an acrylic based PSA can expand the performance window and/or give the system a more robust response to substrates of different surface energy. The use of tackifying resins in acrylic PSAs is a valuable tool for the adhesive formulator. However, the selection of viable candidates is limited.

The polarity of acrylic systems mandates the use of polar tackifying resins to achieve the desired level of compatibility required to enhance the performance of the polymer. Additionally, these polar tackifiers should exhibit similar characteristics as the polymer itself in terms of color, aging stability and UV resistance. The formulator must be sensitive to these requirements so as to not adulterate the polymer with a resin lacking these inherent performance attributes.

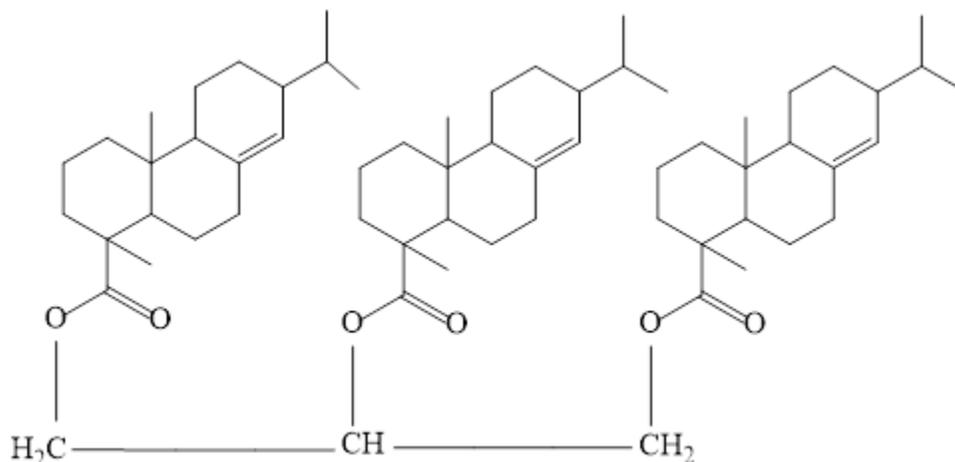
Highly hydrogenated esters of rosin exhibit suitable characteristics for the tackification of acrylic based PSAs. These resins possess the desired level of polarity essential in achieving excellent compatibility with the polymer. The UV and oxidative stability of highly hydrogenated rosin derivatives are complementary to that of the acrylics and they also exhibit suitable softening points for the formulation of pressure sensitive adhesives. Their long-term durability in demanding exterior applications has been demonstrated for decades and these resins require very broad FDA approvals.

The glycerol ester of highly hydrogenated rosin is the industry standard and the global benchmark for tackified acrylic based PSAs. This rosin derivative typically exhibits a 80°C softening point. The pentaerythritol ester of highly hydrogenated rosin is also available and used to a much lesser extent due to its higher softening point of 100°C. Partially hydrogenated glycerol esters are generally excluded from consideration due to their lack of oxidative stability, retention of properties and darker color. Although the glycerol ester of highly hydrogenated rosin is a versatile and widely used tackifier for acrylic based PSAs, its utility in some applications may be limited due to its softening point.

Table 1. Esters of Highly Hydrogenated Rosin – Typical Properties

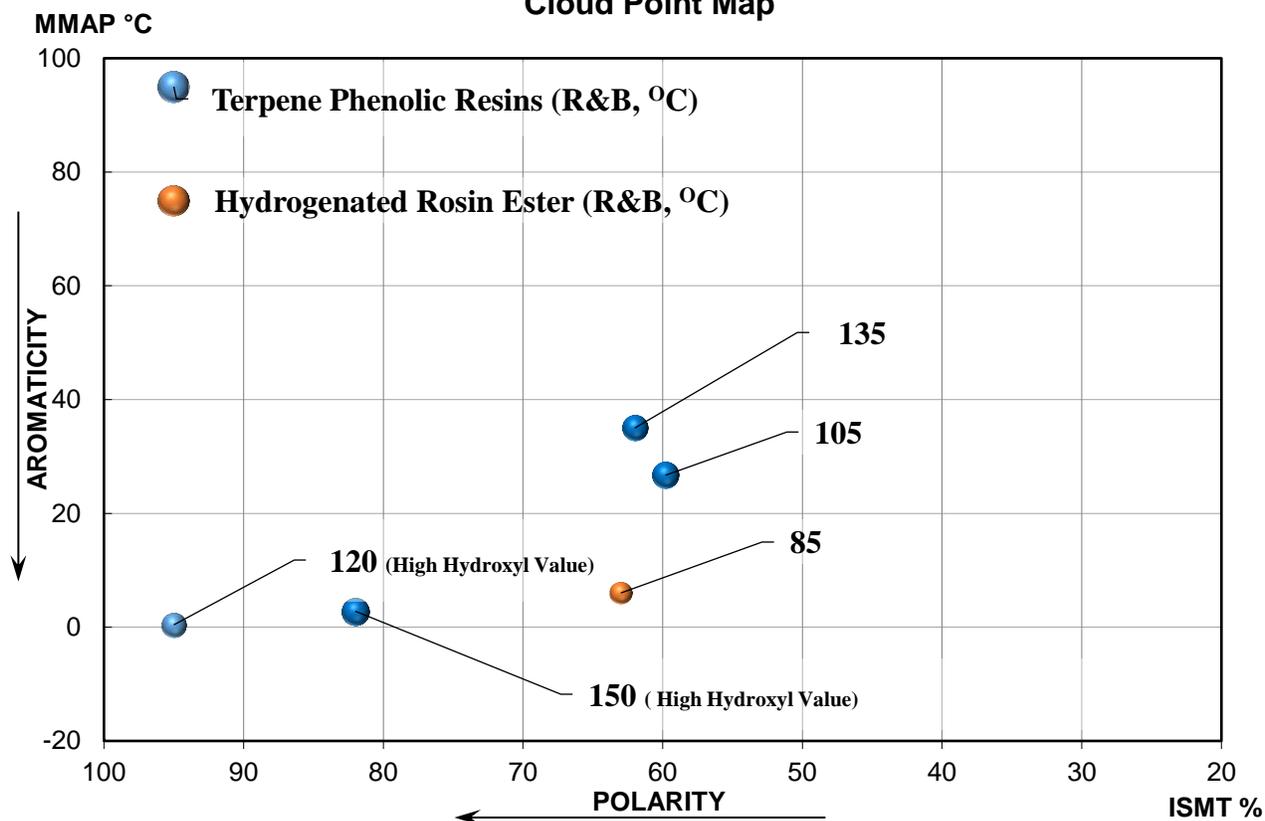
Rosin Ester Type	Softening Point R&B, °C	Acid Number	Color Gardner, Neat
Glycerol Ester of Highly Hydrogenated Rosin	80	6	2
Pentaerythritol Ester of Highly Hydrogenated Rosin	100	10	4

Figure 1. Generic Structure – Glycerol Ester of Hydrogenated Rosin



As previously stated, a limited number of tackifiers exhibit the required degree of polarity and compatibility with acrylic PSA polymers. In addition to highly hydrogenated rosin derivatives, terpene phenolic resins exhibit sufficient polarity and corresponding compatibility to effectively tackify traditional acrylic PSAs. In Figure 2, the relative polarity of these tackifiers is mapped.

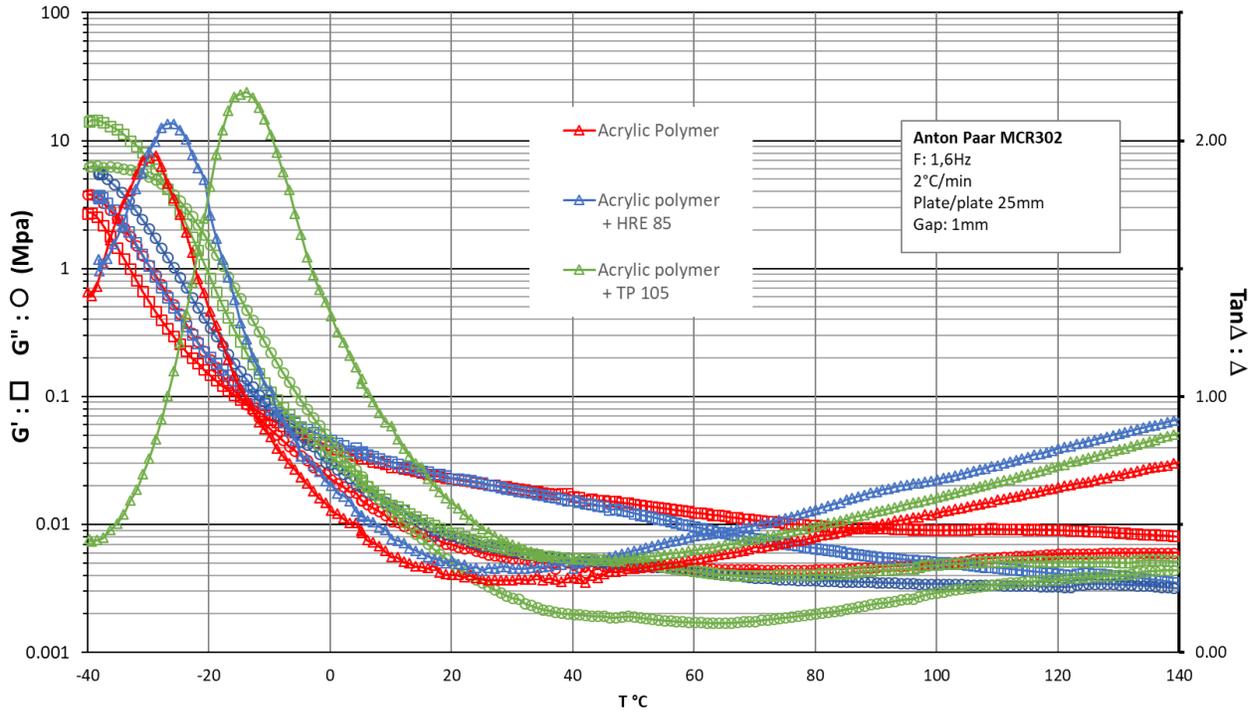
Figure 2. Cloud Point Graph
Cloud Point Map



MMAP = Mixed Methylcyclohexane Aniline Cloud Point in °C
ISMT% = Methanol Cloud Point, normalized to %

The proximity of terpene phenolic resins and the glycerol ester of highly hydrogenated rosin is clearly evident in the cloud point map. Based on this information and corresponding DMA data in Figure 3, compatibility between acrylic polymers and terpene phenolic resins can be validated. This validation is evident from the convergence of the T_gs of the polymer and tackifier resin to afford one T_g for the resulting adhesive.

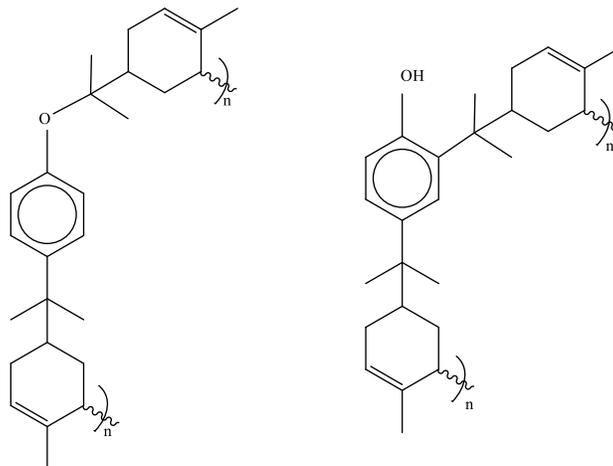
Figure 3. DMA Validation Graph
Dynamic Mechanical Analysis



Terpene phenolic resins are produced by the Lewis acid catalyzed (usually boron trifluoride or one of its complexes such as diethyl ether or acetic acid) reaction of monoterpenes with phenol. By controlling the stoichiometry of the terpenes and phenol, it is possible to engineer a wide variety of resins with a broad range of compatibility with acrylics, and with a broad range of glass transition temperatures and molecular weights. Within limits, it is possible to vary these properties independently to achieve finely tuned adhesive systems.

For PSAs, softening points of 95-120 °C are used routinely. These resins can be produced with varying amounts of free hydroxyl groups, with hydroxyl values ranging from about 30 up to about 150. Two generic terpene phenol structures are illustrated in Figure 4 below.

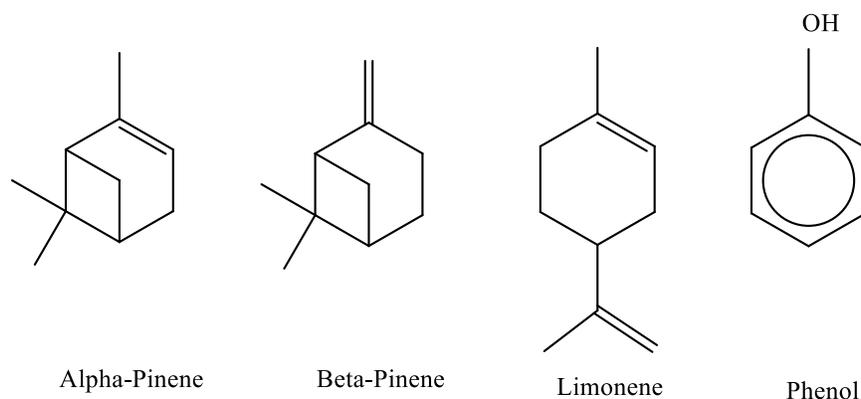
Figure 4. Terpene Phenol Structures



The performance of acrylic based PSAs can be enhanced by the utilization of a suitable terpene phenolic resin, alone or as a co-tackifier with a highly hydrogenated rosin ester. Terpene phenolic resins possess two characteristics which make this a formulating option. First, they are very polar when compared to unmodified polyterpene and hydrocarbon resins and can be chemically altered to be more polar than highly hydrogenated rosin esters when desired. Secondly, terpene phenolic resins can tackify acrylics by means of hydrogen bonding, this being in addition to bulk tackification via mixing. Consequently, it is possible to formulate PSAs with robust shear, tack, and peel strength when formulating with terpene phenolic resins.

Terpene phenolic resins can be manufactured from alpha-pinene, beta-pinene, and d-limonene. These pinenes are sourced from pine trees in the form of crude sulfate turpentine (kraft paper process), gum turpentine and wood turpentine. The actual amounts of these terpenes are highly dependent on the species of pine tree, and the method of turpentine production. D-limonene is also available as a by-product of the orange juice industry. These terpene phenolic resins are renewable and bio-based making their composition greater than 70% bio-based carbon.

Figure 5. Terpene Monomer Structures and Phenol



Many derivatives of phenol can be used to produce terpene phenolic resins, but phenol is preferred due to the rigidity of the repeat units and the ability to vary polarity (hydroxyl functionality) over a broad range.

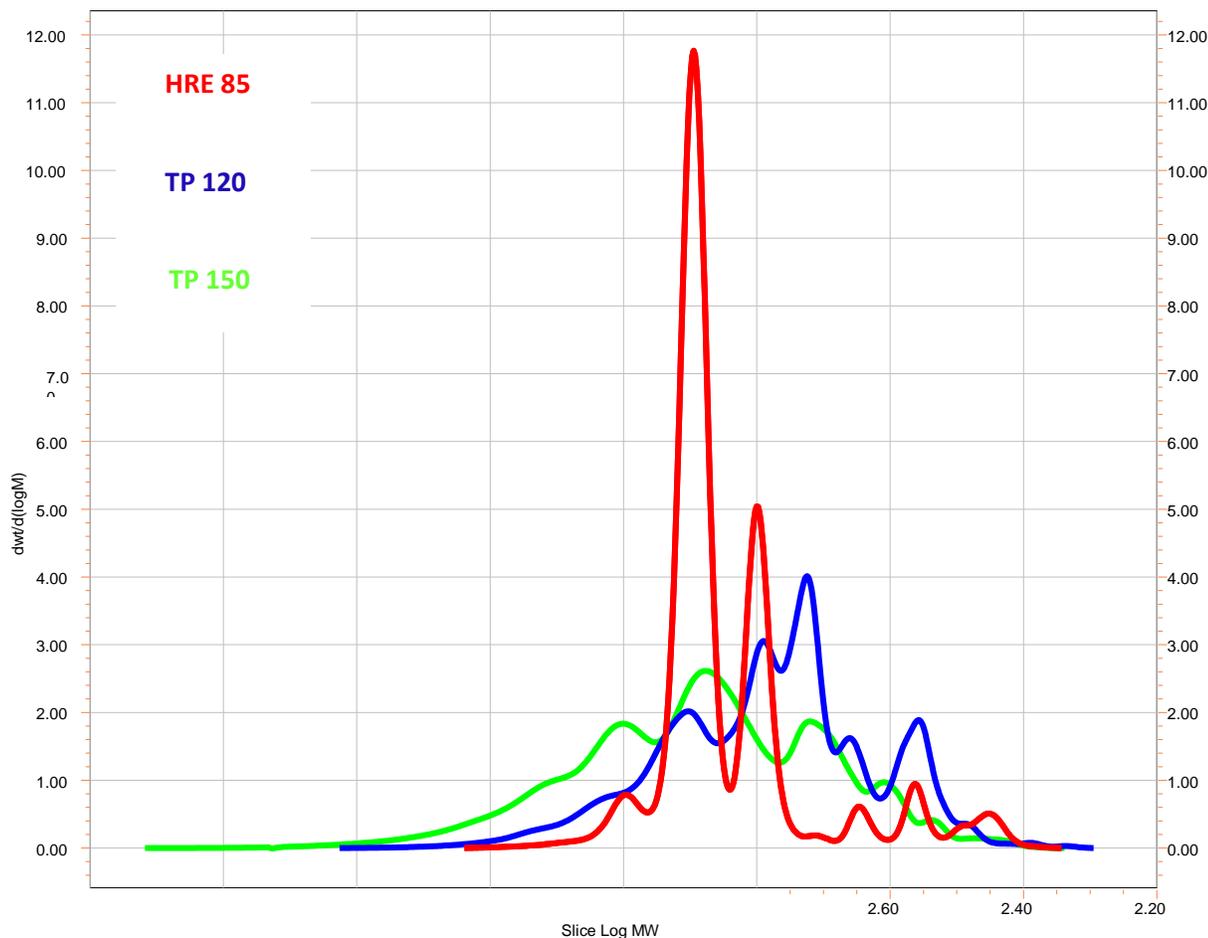
Terpene phenolic resins can be offered in a range of softening points and hydroxyl values. By manipulating these two variables, a much wider product offering is available to the adhesive formulator. The following table exemplifies a range of generic terpene phenolic resins commercially available.

Table 2. Comparative Resin Table**Comparative Resin Table**

Resin	Color (Gardner 50/50 toluene)	R&B SP (°C)	Acid Value (mg KOH)	Hydroxyl Value (mg KOH/g)	Mn	Mw	Mz	Tg Onset (°C)	Tg Midpoint (°C)
HRE 85	1	82	6	<1	666	718	755	27	32
TP 105	3.8	105	<1	-	579	791	1105	47	54
TP 120	3.1	118	<1	156	637	734	859	63	71
TP 135	3.9	131	<1	26	720	850	1010	75	82
TP 150	5.2	149	<1	99	805	966	1178	96	104

In addition to the attributes of softening point and hydroxyl numbers, the molecular weight profile of terpene phenolic resins differs from that of highly hydrogenated rosin esters. This is shown by the molecular weight distribution graph in Figure 6. This difference can significantly improve the overall performance of an acrylic system when compared to one containing a hydrogenated rosin ester.

Figure 6. Molecular Weight Data



In addition to the range of softening points made available when using terpene phenolic resins, pressure sensitive properties can be enhanced, specifically adhesion to low energy substrates.

Although acrylic based PSAs have outstanding adhesion and shear strength, they have some deficiencies such as poor adhesion to low energy surfaces such as polyethylene and polypropylene. A number of solutions have emerged over the years to mitigate this problem. Surface treatment of problematic films such as polyethylene and polypropylene with radiation afford a more polar surface is one example that has been used commercially. Additionally, new types of acrylic polymers have been formulated which incorporate more hydrophobic alkyl groups on the acrylate monomers to enhance anchorage to these polyolefin substrates. Lastly, new tackifiers or tackifier combinations have been developed with varying degrees of success to improve adhesion.

Hydrogenated rosin esters and terpene phenol resins have been used successfully to tackify acrylics to provide enhanced adhesion to non-polar substrates without significant compromise of the overall balance of adhesive properties.

Hydrogenated rosin ester performance is improved due to the hydrophobicity of the resin. The hydrophobicity is significantly increased while still allowing the polar sections of the esters to afford good tackification. Moreover, significant improvement in oxidation resistance is also achieved due to the high degree of hydrogenation. This results in lighter color rosin esters which remain stable for longer periods of time. Rosin can be hydrogenated to varying degrees depending on desired performance properties.

Similarly, terpene phenolic resins can be designed with varying levels of hydrophobic/hydrophilic sections to achieve the same desirable balance of adhesion to non-polar substrates and tackification of the various acrylic polymers. This can be done without significant compromise of important properties such as molecular weight, softening point and hydroxyl value.

In compounded acrylic PSA systems, relatively low resin loadings (20%) can shift the performance window and response factors significantly. Validation using DMA and conventional adhesive testing indicates tackification of the acrylic polymer is a very simple and commercially viable process for enhancing the performance of the base polymer. This formulating tool is very versatile and when properly paired the acrylic polymer and tackifying resin combination synergistically contributes to the overall performance of the adhesive.

The performance of a commercial acrylic polymer tackified separately with a 75°C softening point highly hydrogenated rosin ester and two higher softening point terpene phenol resins was tested using standard PSTC test methods. Testing was performed on stainless steel, a very polar substrate, and low density polyethylene, a very non-polar substrate, these results are presented in Table 3 and the bar charts that follow.

The highly hydrogenated rosin ester imparted a significant improvement in both tack and peel to the polyethylene substrate relative to the acrylic polymer alone. One of the performance issues with acrylics is their poor adhesion to non-polar substrates. This deficiency can be remedied by the use of highly hydrogenated rosin esters.

The terpene phenolic resins also imparted significant improvements in adhesion across the board, and without significant reduction in shear properties. This phenomenon is not typical in tackified adhesives. This is attributed to the high softening points of the terpene-phenol resins coupled with the combination of aliphatic, aromatic and hydroxyl containing groups.

The results show significant improvements in peel and tack to both stainless steel and polyethylene and with shear values comparable to or exceeding that of the acrylic polymer alone. Similarly, the shear adhesion failure temperatures of the adhesives tackified with the terpene phenolic resins are comparable to, or equal to the acrylic polymer itself.

Table 3. PSA Testing Data Summary

PSA TESTING DATA SUMMARY

	PEEL 180° SS (PSTC 101) N/inch	PEEL 180° LDPE/NT (PSTC 101) N/inch	LOOP SS (PSTC 16) N/inch	LOOP LDPE/NT (PSTC 16) N/inch	SHEAR SS (min) (PSTC 107)	SAFT (°C) (PSTC 17)
	dwel time 20 mn	dwel time 20 mn	F average F max	F average F max	1"x1" 1Kg 23°C	1"x1" 0.5Kg
Acrylic Polymer	13.6 ±1.0 AF/CP	1.8 ±0.4	15.3 ±0.7 15.8 ±0.8	1.1 ±0.1 1.2 ±0.1	160	75
Acrylic polymer + RE 85 <i>Sligh cloudy aspect</i>	14.4 ±0.8 AF/CP	6.2 ±0.1	14.1 ±0.5 15.1 ±0.6	5.8 ±0.3 5.9 ±0.3	99	65
Acrylic polymer + HRE 85 <i>cloudy aspect</i>	11 ±0.1 Slight PS	7.9 ±0.4	8.5 ±0.7 9.3 ±0.9	3.5 ±0.2 4.1 ±0.4	82	60
Acrylic polymer + TP 105	17.6 ±0.2 AF/CP	8.5 ±0.3	25.4 ±0.4 26 ±0.3	9.9 ±0.2 9.4 ±0.3	144	68
Acrylic polymer + TP 120	18.2 ±0.9 AF/CF	5.8 ±0.6 slight slip-stick	24.8 ±1.7 26.2 ±2.2	8.7 ±0.2 9 ±0.2	377	77

AF: adhesive failure
CF: cohesive failure
CP: clean panel
PS: panel stain

NOTE: 20% resin dry/dry with polymer 50 gsm PET 70 gsm. Drying 15 min at 120°C

Figure 7. Peel Test

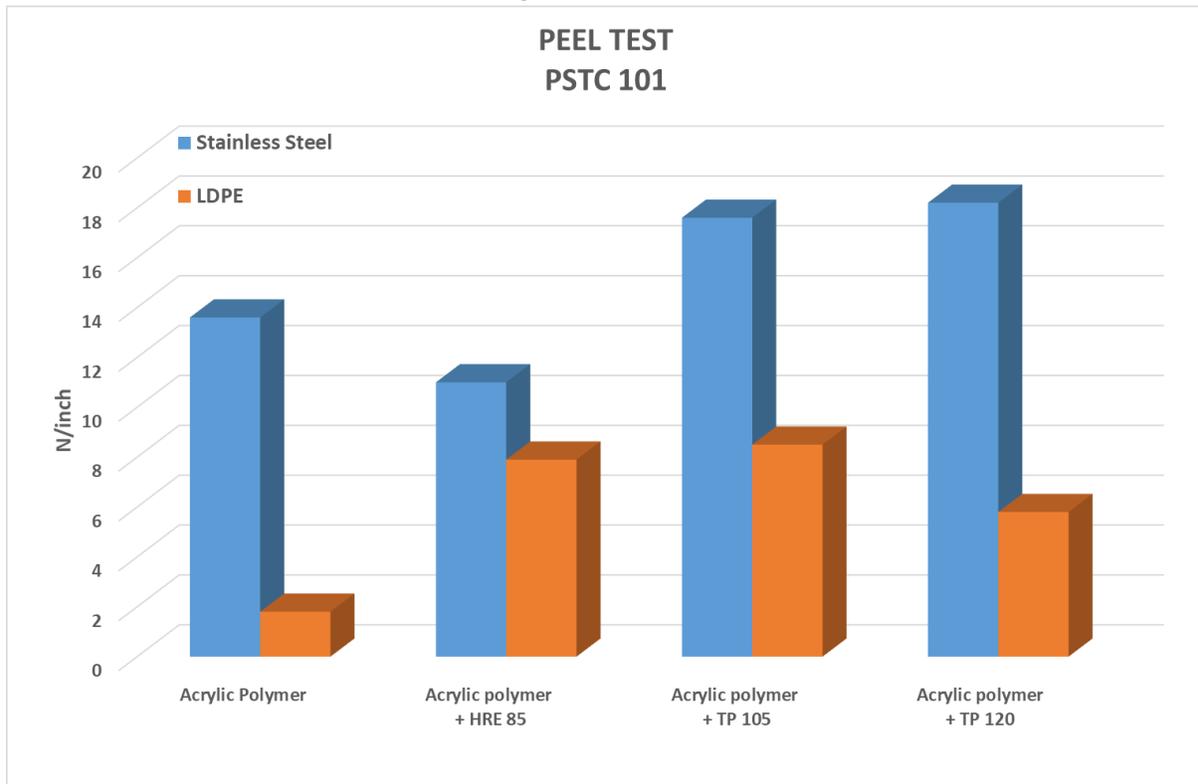


Figure 8. Static Shear

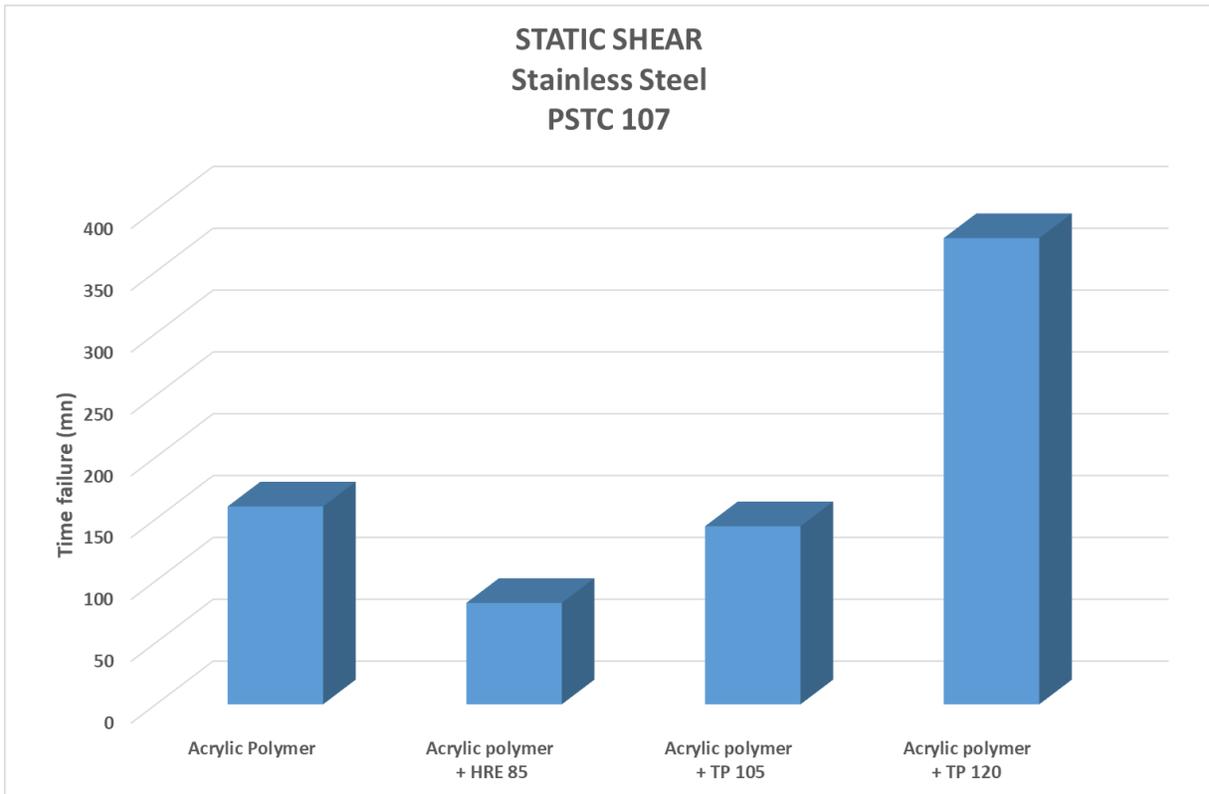


Figure 9. Loop Test

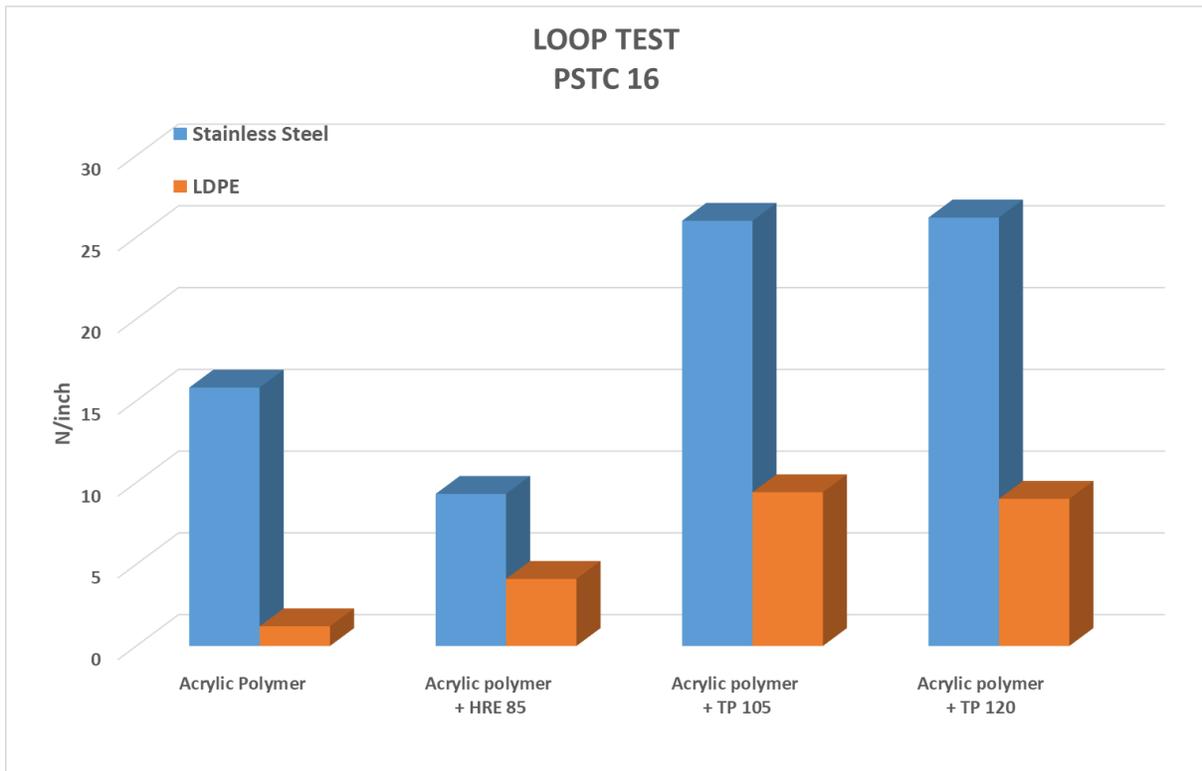
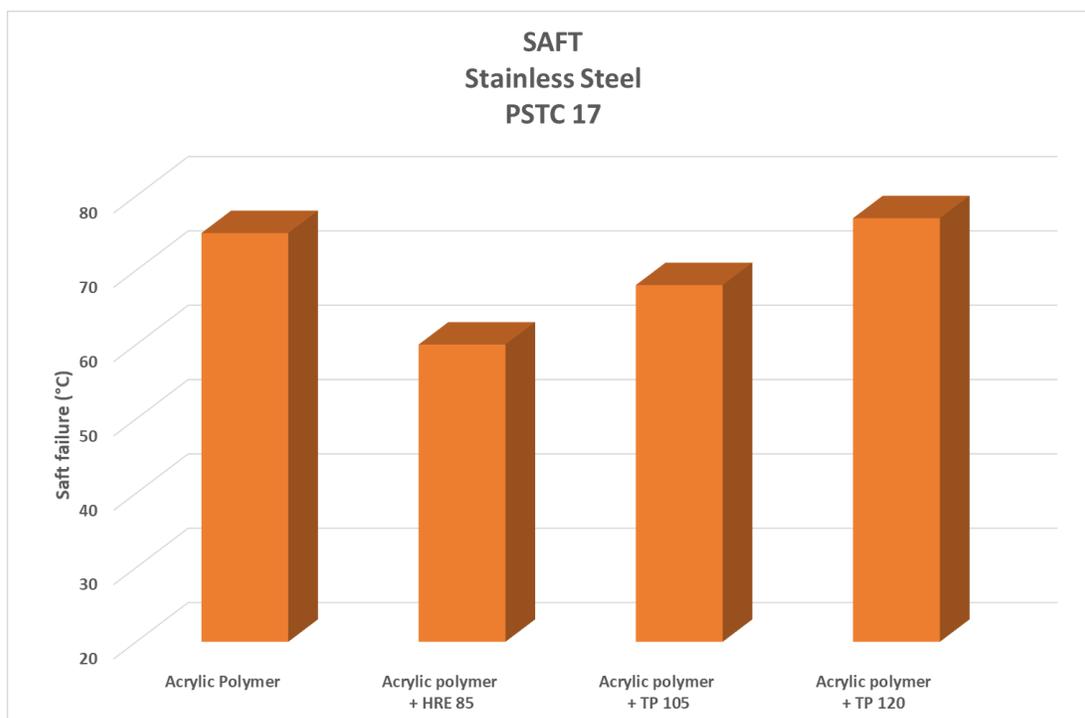


Figure 10. SAFT



In conclusion, highly hydrogenated rosin esters and terpene phenolic resins provide the acrylic PSA formulator with multiple compounding options, both singularly or in combination when performance optimization exceeds the technical limitation of the uncompounded polymer. Specific adhesion enhancements on low energy surfaces as well as the enlargement of the adhesive's performance window can be achieved with the use of these formulary tools. Elevation of SAFT performance is attainable with the use of higher softening point terpene phenolic resins without the traditional loss of tack and substrate wetting. Additionally, more environmentally friendly formulations can be offered due to the high bio-based content of terpene phenolics and highly hydrogenated rosin esters. These resins are all fully adaptable and functional in water-based, solution and hot melt acrylic adhesives.

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