Bio-Based Modified Terpene Resins for Use in UV Cure Acrylate Adhesives

Gregg Patnode, Owner and President of Patnode Adhesive Consulting, LLC, Woodbury, MN

Fumiaki Kisa, Ph.D., General Manager, Innovation Promotion Office, Yasuhara Chemical CO., LTD., Fukuyama, Hiroshima, Japan

Yasushi Tsuura, General Manager, Sales Div., Yasuhara Chemical Co., Ltd., Fuchu City, Hiroshima, Japan

Abstract

When choosing a tackifier for a UV cure acrylate PSA, care must be taken to optimize compatibility, while limiting inhibition of the cure process. In this paper we will review how hydrogenation and modification of polyterpenes can produce bio-based resins compatible with UV cure acrylate systems. The impact of such resins on adhesive properties, resin stability and cure inhibition in UV acrylate systems will be reviewed.

1. Introduction

100% solids, UV cure hotmelt acrylate pressure sensitive adhesives have many advantages (1,2,3,4). Rosin esters, rosins, terpenes and terpene phenols are well known bio-based tackifying resins for many acrylate pressure sensitive adhesives (5,6). However, in 100% solids, UV cure hotmelt acrylate adhesives there are challenges with tackifier solubility and tackifier interference with the UV cure process due to unsaturations in the tackifying resin (7,8,9). These challenges tend to limit the bio-based tackifying options in 100% solids, UV cure hotmelt acrylate adhesives to hydrogenated rosin esters and hydrogenated rosins

In this paper, we investigate the use of hydrogenated terpene phenol resins and hydrogenated, aromatic modified terpene resins as additional bio-based options for tackifying 100% solids, UV cure hotmelt acrylate pressure sensitive adhesives.

2. Experimental Materials and Formulations for Adhesive Testing

To conduct the adhesive performance portion of the study, two UV cure, hot melt acrylate system were used: acResin® A 204 UV and acResin® UV 3532, both from BASF.

The acResin® materials were tackified with the following resins:

(1) Two hydrogenated terpene phenol resin: YS Polyster TH130 and YS Polyster UH115, both from Yasuhara Chemical.

(2) Two hydrogenated, aromatic modified terpene resin: Clearon K105 and Clearon M105, both from Yasuhara Chemical.

(3) Hydrogenated rosin ester: Ester Gum HP from Arakawa Chemical.

(4) Hydrogenated rosin: Foral AX® from DRT.

(5) Hydrogenated hydrocarbon, non bio-based resin: Arkon M100 from Arakawa Chemical.

(6) Non-hydrogenated terpene phenol: YS Polyster T130 from Yasuhara Chemical.

The full list of formulations studied can be found in table 1.

Table 1: Adhesive Formulations

	Hot Melt Acrylate #1	Hot Melt Acrylate #2	Hydrogenated Terpene Phenol - 1	Hydrogenated Terpene Phenol - 2	Aromatic Modified, Hydrogenated Terpene -1	Aromatic Modified, Hydrogenated Terpene -2	Hydrogenated Rosin Ester	Hydrogenated Rosin	Hydrogenated Hydrocarbon	Non Hydrogenated Terpene Phenol
	(acResin® A 204 UV)	(acResin® UV 3532)	(YS Polyster TH130)	(YS Polyster UH115)	(Clearon K105)	(Clearon M105)	(Ester Gum HP)	(Foral AX®)	(Arkon M100)	(YS Polyster T130)
Sample ID	parts	parts	parts	parts	parts	parts	parts	parts	parts	parts
Base HMA #1	100									
Hydrogenated Terpene phenol #1 (10parts)	100		10							
Hydrogenated Terpene phenol #1 (20parts)	100		20							
Hydrogenated Terpene phenol #2 (10parts)	100			10						
Hydrogenated Terpene phenol #2 (20parts)	100			20						
AM Hydrogenated Terpene #1 (5parts)/Hydrogenated Rosin (5parts)	100				5		5			
Hydrogenated Rosin Ester (10parts)	100						10			
Hydrogenated Rosin Ester (20parts)	100						20			
Hydrogenated Rosin (10 parts)	100							10		
Hydrogenated Rosin (20 parts)	100							20		
Terpene phenol (10 parts)	100									10
Terpene phenol (20 parts)	100									20
Base HMA #2		100								
Hydrogenated Terpene phenol #1 (10parts)		100	10							
Hydrogenated Terpene phenol #1 (20parts)		100	20							
Hydrogenated Terpene phenol #2 (10parts)		100		10						
Hydrogenated Terpene phenol #2 (20parts)		100		20						
Hydrogenated, Aromatic Modified Terpene #1 (10parts)		100			10					
Hydrogenated, Aromatic Modified Terpene #1 (20parts)		100			20					
Hydrogenated, Aromatic Modified Terpene #2 (10parts)		100				10				
Hydrogenated, Aromatic Modified Terpene #2 (20parts)		100				20				
Hydrogenated Rosin Ester (10parts)		100					10			
Hydrogenated Rosin Ester (20parts)		100					20			
Hydrogenated Rosin (10 parts)		100						10		
Hydrogenated Rosin (20 parts)		100						20		
Hydrogenated Hydrocarbon (10parts)		100							10	
Hydrogenated Hydrocarbon (20parts)		100							20	
Terpene phenol (10 parts)		100								10
Terpene phenol (20 parts)		100								20

<u>Sample preparation on formulations in table 1</u>

The adhesives in table 1 were prepared by pre-heating the base acrylate adhesive and selected resin in an oven for 2 hours at 100°C to 130°C to soften. The softened mixture was then mixed at temperature for 1 hour. After mixing, the material was allowed to cool and de-gas.

The adhesive mixture was sandwiched between a PET film (25µm) and a release PET film (25µm) and calendared between two temperature-controlled rolls (hot melt #1 adhesives: 90°C roll temperatures; hot melt #2 adhesives: 65°C roll temperatures). While calendaring the adhesive, roll clearance and coating speed were adjusted to achieve a uniform thickness, creating an adhesive thickness of 50µm.

The adhesives were cured using a Fusion UV Lamp System F300S/Benchtop Conveyor LC-6 (Fusion UV System Inc.) with an H-bulb using an Accumulated UV meter: UIT-250/UVD-C254 (USHIO Inc.). All samples exposed to 1200 mJ/cm^2 UV254, except where noted.

3. Adhesive Performance Testing

The peel testing was conducted per ASTM D3330/PSTC 101. Testing was conducted at a peel speed of 300mm/min, peel angle of 180°, and temperature of 23°C.

The tack testing was conducted per JIS Z0237:2009 at a temperature of 23°C.

The holding power test was conducted per ATSM D3665/PSTC 7 with a contact area of 25mm x 25mm and a weight of 1 kg and temperatures of 40°C and 70°C

Table 2: Adhesive Performance Testing Results

	Tack	Peel to SS	Peel to PE	Peel to PP	°C 40 Holding Power	70 Holding Power (1200 mJ)	Failure Mode	70 Holding Power (800 mJ)	Failure Mode
Sample ID	Ball #	N/25mm	N/25mm	N/25mm	min	min		min	
Base HMA #1	7	7.0	0.8	4.0	60	28	adh	49	adh
Hydrogenated Terpene phenol #1 (10parts)	3	8.4	2.7	5.5	60	36.5	adh	55	adh
Hydrogenated Terpene phenol #1 (20parts)	<1	12.6	4.2	7.4					
Hydrogenated Terpene phenol #2 (10parts)	3.0	9.3	4.1	8.3	60	33.5	adh	21	adh
Hydrogenated Terpene phenol #2 (20parts)	<1	9.2	5.3	8.8					
AM Hydrogenated Terpene #1 (5parts)/Hydrogenated Rosin (5parts)	5	8.3	4.1	7.5	60	21	adh	48	adh
Hydrogenated Rosin Ester (10parts)	5	9.3	3.7	6.7	60	50	adh	40.5	adh
Hydrogenated Rosin Ester (20parts)	4	13.4	5.1	9.0					
Hydrogenated Rosin (10 parts)	6	8.8	2.8	7.3	60	12	adh	18.5	adh
Hydrogenated Rosin (20 parts)	7	13.0	4.5	2.9					
Terpene phenol (10 parts)	3	9.5	2.7	5.1	60	60	-	6	coh
Terpene phenol (20 parts)	<1	10.9	3.3	8.2					
Base HMA #2	5	1.3	0.5	1.5					
Hydrogenated Terpene phenol #1 (10parts)	8	3.9	1.9	4.1					
Hydrogenated Terpene phenol #1 (20parts)	5	6.6	3.4	5.8					
Hydrogenated Terpene phenol #2 (10parts)	8	2.7	1.5	3.2					
Hydrogenated Terpene phenol #2 (20parts)	6	6.4	2.6	5.2					
Hydrogenated, Aromatic Modified Terpene #1 (10parts)	7	2.8	1.3	3.4					
Hydrogenated, Aromatic Modified Terpene #1 (20parts)	10	4.7	2.7	5.6					
Hydrogenated, Aromatic Modified Terpene #2 (10parts)	7	3.0	1.6	3.2					
Hydrogenated, Aromatic Modified Terpene #2 (20parts)	8	5.6	3.6	5.8					
Hydrogenated Rosin Ester (10parts)	8	3.3	1.8	3.5					
Hydrogenated Rosin Ester (20parts)	11	6.1	3.5	5.9					
Hydrogenated Rosin (10 parts)	8	2.9	1.4	3.4					
Hydrogenated Rosin (20 parts)	11	4.9	3.1	5.2					
Hydrogenated Hydrocarbon (10parts)	8	3.3	1.7	3.6					
Hydrogenated Hydrocarbon (20parts)	8	6.8	3.2	5.7					
Terpene phenol (10 parts)	8	4.3	2.0	4.0					
Terpene phenol (20 parts)	3	6.8	3.3	6.0					

Discussion of Peel Performance

Figure 1: Peel Adhesion Results for Resins in HMA #1

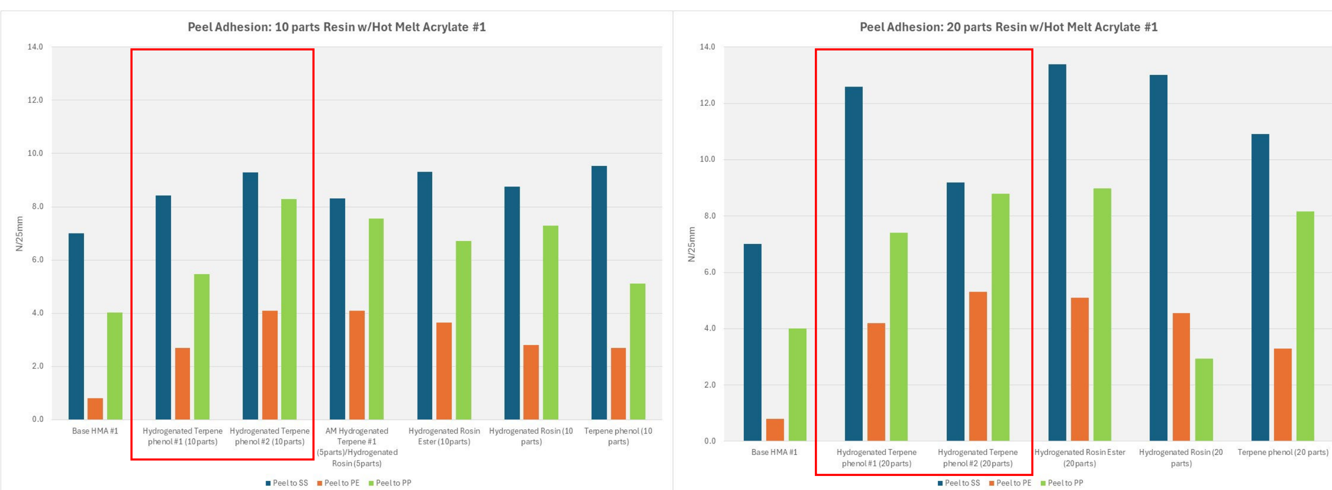


Figure 1 shows peel performance of the various resins at 10 parts and 20 parts in hot melt adhesive #1. When compared to hydrogenated rosin ester and hydrogenated rosin, we observe the hydrogenated terpene phenols can provide comparable peel performance to steel, polyethylene and polypropylene. The hydrogenated, aromatic modified terpene resins were not compatible in HMA #1. Hydrogenated, aromatic modified terpene resin #1 was blended 50:50 with the hydrogenated rosin to provide compatibility. When compared to hydrogenated rosin ester and hydrogenated rosin, we observe at 10 parts total resin, the hydrogenated, aromatic modified terpene mixed with hydrogenated rosin shows comparable adhesion performance to steel, polyethylene and polypropylene. The hydrogenated hydrocarbon was not compatible in HMA #1. The non hydrogenated terpene phenol shows comparable performance to the hydrogenated rosin ester and hydrogenated rosin.

Figure 2: Peel Adhesion Results for Resins in HMA #2

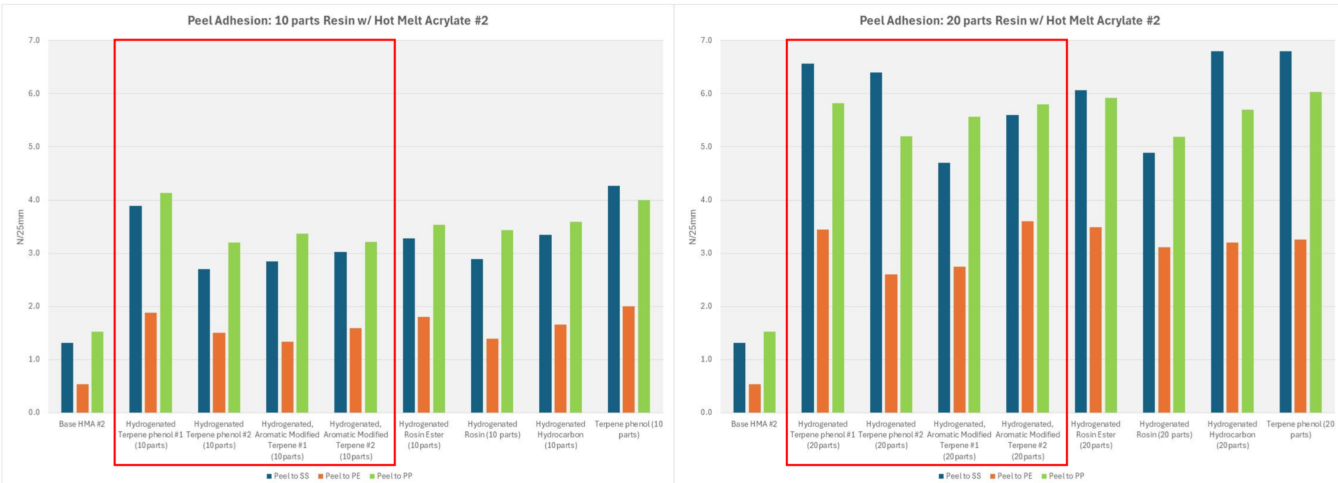
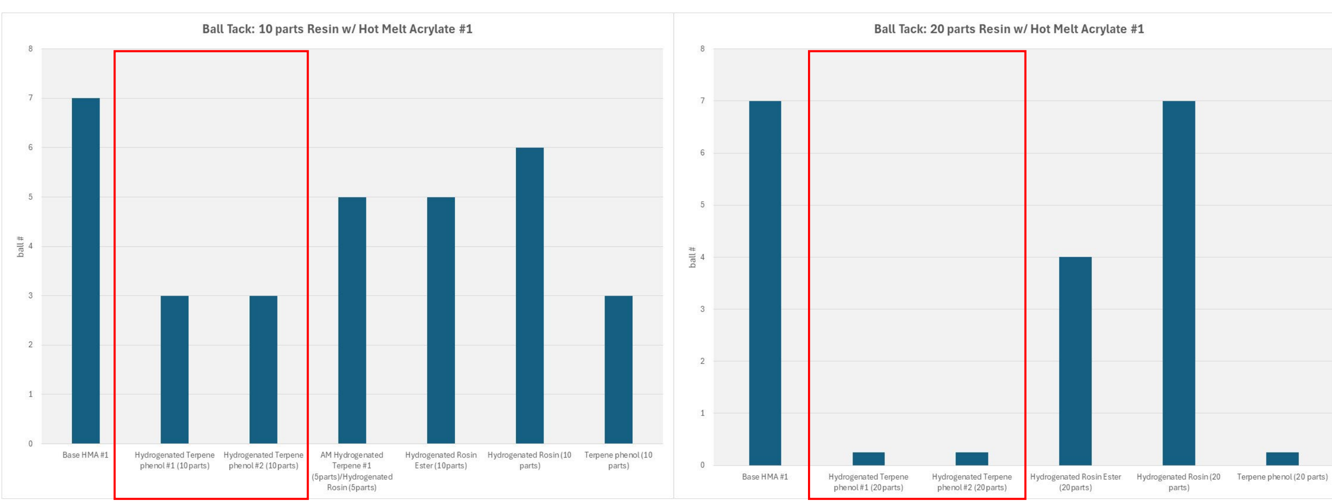


Figure 2 shows peel performance of the various resins at 10 parts and 20 parts in hot melt adhesive #2. When compared to hydrogenated rosin ester and hydrogenated rosin, we observe the hydrogenated terpene phenols can provide comparable performance to steel, polyethylene and polypropylene. When compared to hydrogenated rosin ester and hydrogenated rosin, we observe the hydrogenated, aromatic modified terpenes can provide comparable performance to steel, polyethylene and polypropylene. The hydrogenated hydrocarbon showed comparable peel performance. The non hydrogenated terpene phenol shows comparable performance to the hydrogenated rosin ester and hydrogenated rosin.

<u>Discussion of Tack Performance</u>

Figure 3: Tack Performance for Resins in HMA #1



The Ball Tack Test (JIS Z0237:2009), is similar to the Rolling Ball Tack Test (ASTM D3121/PSTC 6). In the Ball Tack Test, steel balls of different sizes are rolled down a ramp and across the adhesive. The largest ball that stops on the adhesive is recorded. Ball sizes are numbered 1 through 32. Ball #1 is 0.8 mm in diameter. Each number signifies an increase in diameter of 0.8 mm, ball #32 has a diameter of 25 mm. The larger the number, the higher the tack.

Figure 3 shows tack performance of the various resins at 10 parts and 20 parts in hot melt adhesive #1. We observe the hydrogenated terpene phenols show lower tack compared to the hydrogenated rosin ester and hydrogenated rosin. As mentioned in the peel adhesion discussion, the hydrogenated, aromatic modified terpene resins were not compatible in HMA #1. Hydrogenated, aromatic modified terpene resin #1 was blended 50:50 with the hydrogenated rosin to provide compatibility. When compared to hydrogenated rosin ester and hydrogenated rosin, we observe at 10 parts total resin, the hydrogenated, aromatic modified terpene mixed with hydrogenated rosin shows comparable tack. The hydrogenated hydrocarbon was not compatible in HMA #1. The non hydrogenated terpene phenol shows lower tack to the hydrogenated rosin ester and hydrogenated rosin at both loadings.

Figure 4: Tack Performance for Resins in HMA #2

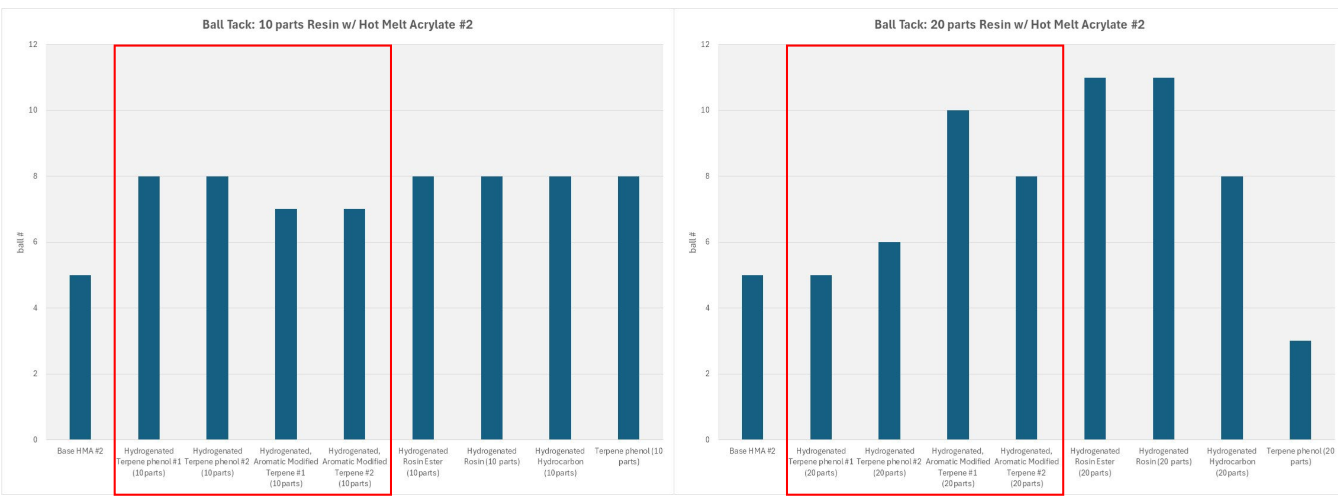
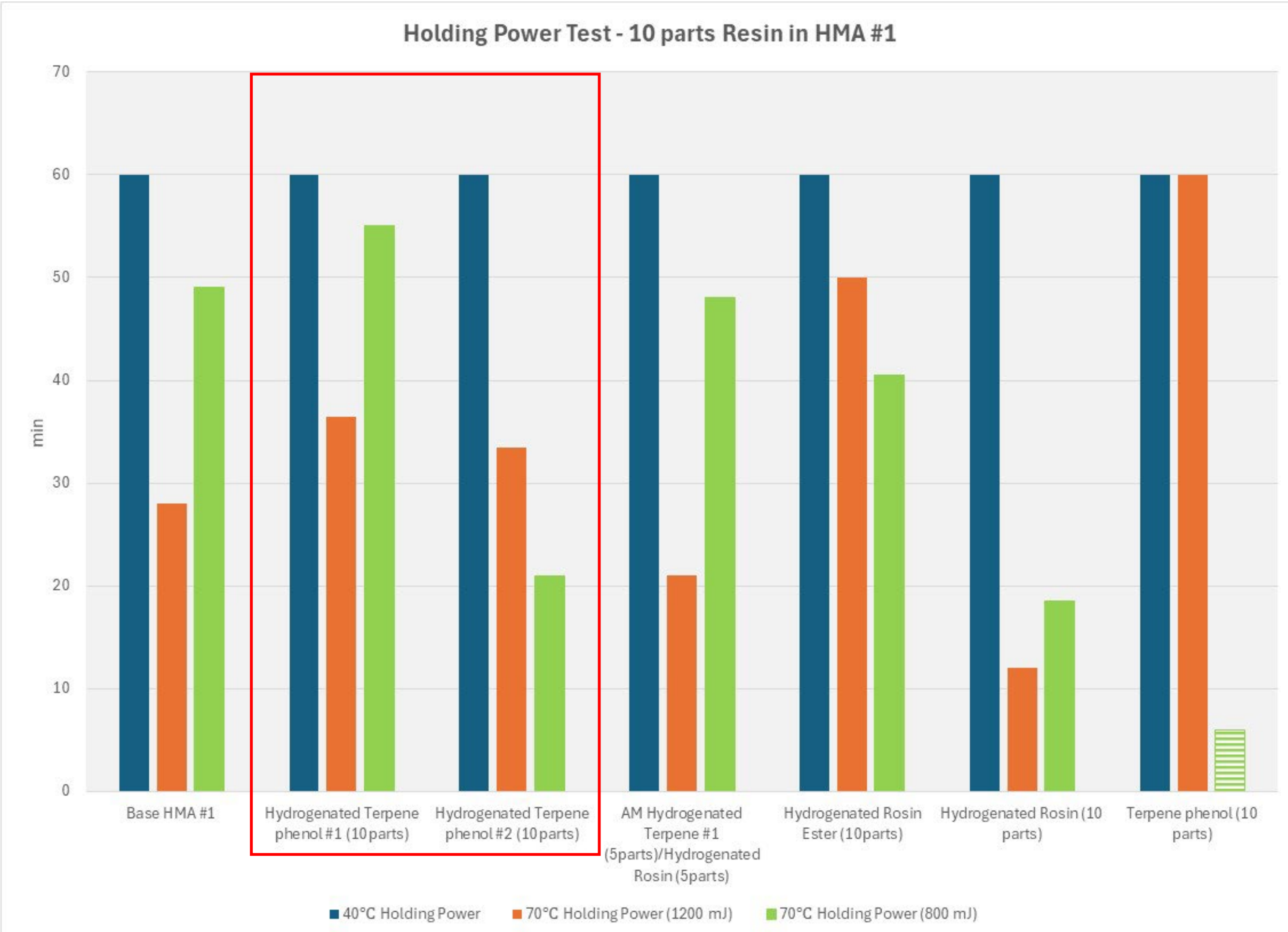


Figure 4 shows tack performance of the various resins at 10 parts and 20 parts in hot melt adhesive #2. We observe the hydrogenated terpene phenols can provide comparable tack to the hydrogenated rosin ester and hydrogenated rosin at 10 parts and reduced tack at 20 parts. The aromatic modified terpenes can provide comparable tack to the hydrogenated rosin ester and hydrogenated rosin. The hydrogenated hydrocarbon can provide comparable tack performance. The non hydrogenated terpene phenol shows comparable tack to the hydrogenated rosin ester and hydrogenated rosin at 10 parts, and reduced tack at 20 parts.

Discussion of Holding Power Performance

Figure 5: Holding Power Performance for Resins in HMA #1



The holding power performance at 40°C did not show any difference in resin type. All materials had no failure or movement after 60 minutes. At 70°C differences were observed. All materials, except the non-hydrogenated terpene phenol, failed before 60 minutes. However, the failure mode in all cases was adhesive to steel panel. The adhesive did not fail cohesively, therefore conclusions regarding impact on cure cannot be made. To attempt to observe differences in cohesive strength based on resin type, the test was repeated with UV cure lowered to 800 mJ. At the lower cure, cohesive failure was only observed with the non-hydrogenated terpene phenol, all other failure was adhesive to steel panel. Based on the results, conclusions regarding interference with UV cure cannot be made.

Summary of adhesion testing results:

The data outlined above shows hydrogenated terpene phenols are viable candidates for use in UV cure acrylate adhesives as they provide the potential for comparable adhesion, tack and holding power to hydrogenated rosin ester and hydrogenated rosin. The data shows hydrogenated, aromatic modified terpene resins have some compatibility limits depending on the chemistry (polarity) of the base UV cure acrylate adhesive. The data shows when hydrogenated, aromatic modified terpene resins are compatible in a UV cure acrylate adhesive they can provide comparable adhesion, tack and holding power to hydrogenated rosin ester and hydrogenated rosin.

4. UV Cure Inhibition

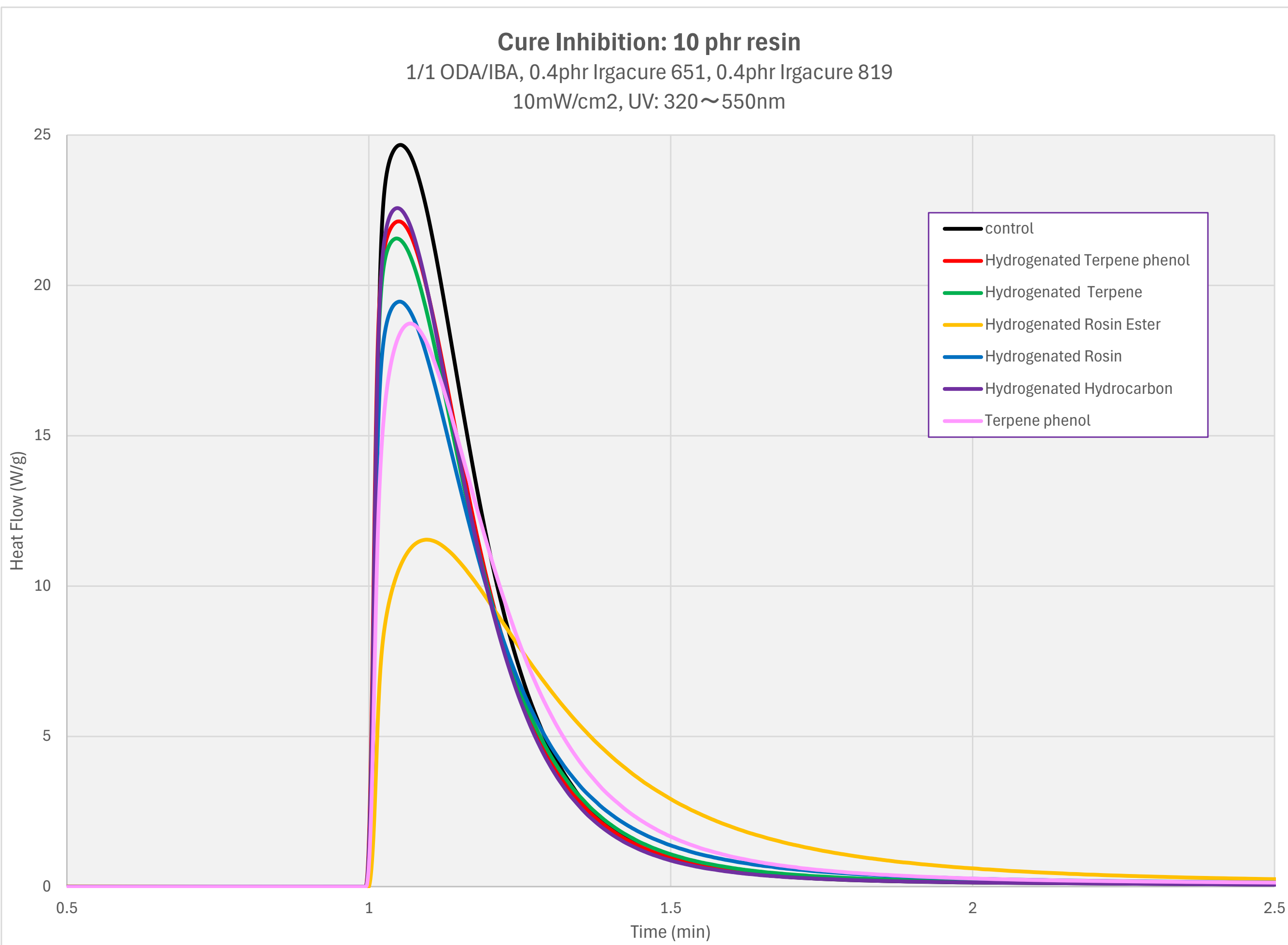
The holding power test did not show differences in the performance of the hydrogenated materials. To isolate impact of resin type of UV cure, Photo-DSC testing was completed on the formulations outlined in table 3.

Table 3: Formulations for UV Inhibition Testing

	Monomer #1	Monomer #2	Photo initiator #1	Photo initiator #2	Hydrogenated Terpene Phenol	Aromatic Modified, Hydrogenated Terpene	Hydrogenated Rosin Ester	Hydrogenated Rosin	Hydrogenated Hydrocarbon	Non Hydrogenated Terpene Phenol
	Octadecyl acrylate	Isobornyl acrylate	IRGACURE® 819	IRGACURE® 651	(YS Polyster TH130)	(Clearon K105)	(Ester Gum HP)	(Foral AX®)	(Arkon M100)	(YS Polyster T130)
Sample ID	parts	parts			parts	parts	parts	parts	parts	parts
Control	50	50	0.4	0.4						
Hydrogenated Terpene phenol	50	50	0.4	0.4	10					
Hydrogenated, Aromatic Modified Terpene	50	50	0.4	0.4		10				
Hydrogenated Rosin Ester	50	50	0.4	0.4			10			
Hydrogenated Rosin	50	50	0.4	0.4				10		
Hydrogenated Hydrocarbon	50	50	0.4	0.4					10	
Terpene phenol	50	50	0.4	0.4						10

The testing was run using a TA Instruments Universal V4.5A TA Instruments at 10mW/cm2, UV: 320～550nm.

Figure 6: Photo-DSC results



The photo-DSC data indicates the hydrogenated terpene phenol and hydrogenated, aromatic modified terpene have minimal impact on UV generated free radicals at 320～550nm and should provide comparable or improved inhibition results compared to hydrogenated rosins ester and hydrogenated rosin.

5. Stability

An area of concern for bio-based materials can be stability. The stability of hydrogenated terpene phenol resins and hydrogenated, aromatic modified terpene resins were compared to that of hydrogenated rosin ester and hydrogenated rosin. This was done by exposing resins to elevated temperatures and measuring color change and oxidative degradation. The materials and testing results are shown in table 4.

The color testing was conducted by exposing the materials to 180°C in air for 6 hours.

The Chemiluminescence testing was conducted using a Chemiluminescence Analyzer CLA-FS-4 (Tohoku Electronic Industrial Co., LTD.). Resins were exposed to 180°C in air for 6 hours prior to testing. The samples were then tested from room temperature to 80°C, with total count indicative of oxidative degradation.

Table 4: Materials and Aging Results

	Hydrogenated Terpene Phenol #1	Hydrogenated Terpene Phenol #2	Hydrogenated, Aromatic Modified Terpene	Hydrogenated Rosin Ester	Hydrogenated Rosin	Hydrogenated Hydrocarbon	Non Hydrogenated Terpene Phenol
	(YS Polyster TH130)	(YS Polyster UH115)	(Clearon K105)	(Ester Gum HP)	(Foral AX®)	(Arkon M100)	(YS Polyster T130)
Bromine Value (measured) gBr2/100g resin	17.5	8.9	9.3	54.7	46.5	<8	23.4
Acid Value (measured) KOHmg/g	<5	<5	<5	16.5	167.8	<5	<5
OH Value (measured) KOHmg/g	33.9	16.9	40	52.4	40.6	<5	40
Initial Color (Gardner)	<1	<1	<1	7.5	<1	<1	6
6hr, 180C Color (Gardner)	5.2	3.3	<1	9.7	7.5	<1	9
Chemiluminescence (total count 10^5)	9.9	6.3	9.8	54.4	18.8	4.9	15.3

Figure 7: Heat Exposure Color Change

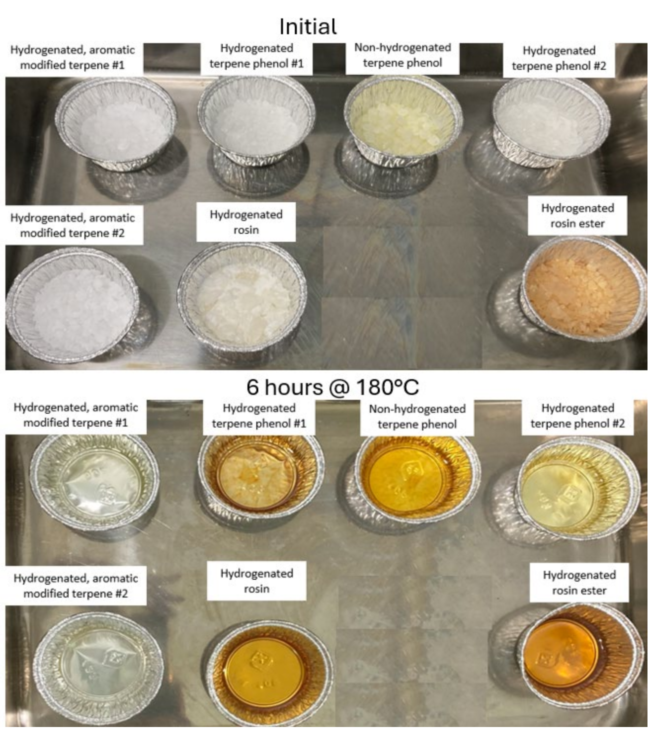
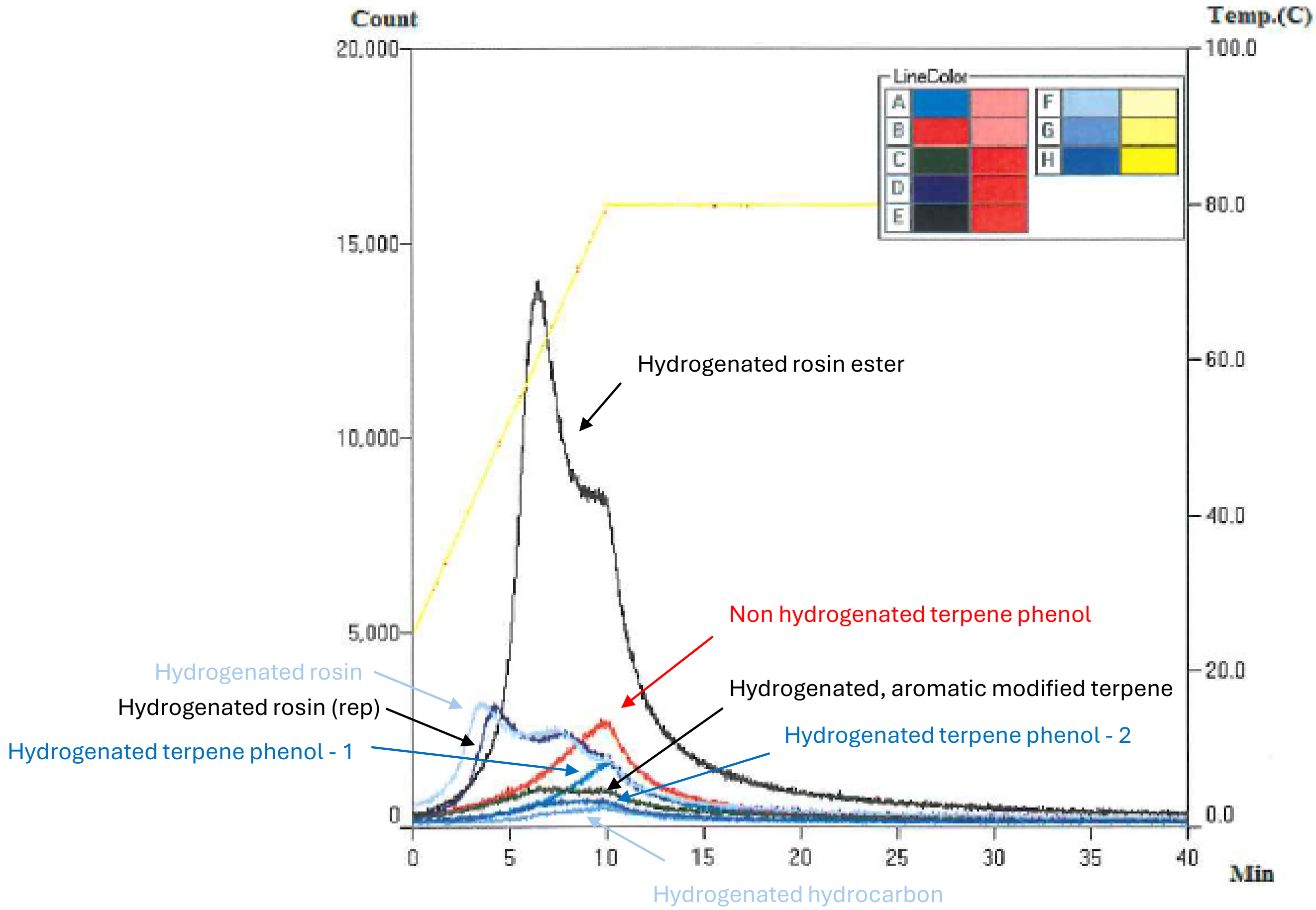


Figure 8: Chemiluminescence after 6 hours @ 180°C



Discussion of Heat Stability Testing:

The color change and chemiluminescence data shows hydrogenated terpene phenol resins have equivalent, or possibly an improved, stability compared to hydrogenated rosin ester and hydrogenated rosin. The color change and chemiluminescence data shows the hydrogenated, aromatic terpene resin has improved stability compared to hydrogenated rosin ester and hydrogenated rosin.

6. Conclusion

Hydrogenated terpene phenol resins and hydrogenated, aromatic modified terpene resins are two bio-based materials that offer additional options for tackifying UV cure acrylate adhesives.

Hydrogenated terpene phenol resins have the capability to offer performance, stability, compatibility, and UV inhibition equivalent perrformance when compared to a hydrogenated rosin ester or hydrogenated rosin.

Hydrogenated aromatic modified terpene resins have lower compatibility in UV cure acrylate adhesives. However, in those systems in which they are compatible, they can offer performance and UV inhibition equivalent to a hydrogenated rosin ester or hydrogenated rosin. In those systems in they are compatible, hydrogenated aromatic modified terpene resins can offer improve stability compared to hydrogenated rosin ester or hydrogenated rosin.

7. Literature References:

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