Acrylic Pressure Sensitive Adhesives Exhibiting Enhanced Adhesion to Low Surface Energy Substrates.

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Abstract

Prevailing trend towards the use of lighter and lower cost engineered plastics in automotive, construction, aerospace, electronics and other industrial end uses have created a need for pressure sensitive materials that can bond well to these new, inherently low surface energy plastics. Reported herein are novel all acrylic compositions with inherently lower surface energy that display significantly improved adhesion to low surface energy substrates such as polyethylene and polypropylene. Additionally, evidence will be presented herein, where these new compositions demonstrate compatibility with tackifiers historically known to be incompatible with more traditional acrylic pressure sensitive polymers.

Introduction

Pressure sensitive polymer compositions have been utilized for well over 50 years. Many types of polymers can be made pressure sensitive via various formulation methods. (Meth)acrylic copolymers are one of the most widely used polymer classes for the production of pressure sensitive adhesives because they are relatively low cost, thermally and oxidatively stable, optically clear, and require little to no formulation to be a useful pressure sensitive material.

There exists a wide variety of (meth)acrylic monomers of which pressure sensitive copolymers can be made. The large selection of available monomers enables a vast range of viscoelastic performance characteristics. Various chemically functional monomers provide a diverse selection of cross-linking options that can be tailored to specific applications.

(Meth)acrylic copolymers can be polymerized and used industrially in a water-borne, solvent cast, melt, or monomer polymer syrups. Any of these formats of delivery can be selected depending on final adhesive performance required, the manufacturing assets available and cost requirements. Many high performance applications require the improved coat quality, coating thickness and material properties achievable via solvent cast, or melt and syrup techniques.

Historically (meth)acrylic pressure sensitive adhesives (PSAs) have delivered adequate adhesion to a broad base of materials used in the industry. Ever evolving trends in the market place have seen, and continue to see the replacement of metal, glass and wood assembly or construction materials with lower cost, lower weight plastic alternatives. This continuing trend toward lighter weight, lower cost materials has challenged the traditional acrylic pressure sensitive adhesives ability to adhere to these new substrates because in most cases these new materials are much lower surface energy (LSE) than traditional materials.

Traditional acrylic pressure sensitive adhesives adhere very well to relatively polar substrates such as steel, aluminum, tin, glass, and wood. These types of materials tend to have higher free surface energy or surface tension than that of the pressure sensitive adhesive as seen in Figure 1. [1]

Material	Surface Energy (dynes/cm)
Tin	526
Aluminum	840
Zinc	852
Silica Glass	~1000
Copper	1362
Stainless Steel	650-1200
Common Acrylic PSA	35-45

Figure 1. Surface energy of various materials and common PSA.

Given the fact that an adherend must have higher surface energy than the corresponding adherent, the common acrylic PSA has no difficulty wetting the materials in Figure 1 to form a bond surface. These types of materials have been or are continuing to be replaced in new material construction in various applications including, automotive assembly, building and construction, electronics and medical devises. Many of these market areas are moving toward lighter weight and often lower cost plastic materials, but still require PSAs to bond various components. These lighter weight plastic components can be challenging to adhere to because they are generally much lower in surface energy as seen in Figure 2.[1]

Material	Surface Energy (dynes/cm)
Polyterafluroethylene	19
Polydimethyl Siloxane	23
Natural Rubber	24
Polyethylene	30
Polypropylene	30
Acrylonitrile Butadiene Styrene	35
Polymethylmethacrylate	41
Polytheylene Terephthalate	42
Polycarbonate	46
Common Acrylic PSA	35-45

Figure 2. Useful plastic materials surface energy compared to common acrylic PSA

As mentioned previously there exist a wide variety of (meth)acrylic monomers to select from when designing an acrylic pressure sensitive adhesive. These materials can be fairly polar or non-polar depending on the length and chemical nature of the ester side chain. A monomers polarity can be expressed as solubility parameter[2] $(cal/cm^3)^{1/2}$ and selecting monomer with lower solubility parameters will result in a final adhesive that can wet lower surface energy materials. Some common acrylic base monomers, functional monomers and polar and non-polar glass transitions temperature (T_g) modifying monomer and their corresponding glass transition temperatures and solubility parameters can be found in Figure 3. [3]

Use	Monomer	T_g	Solubility Parameter $(cal/cm^3)^{1/2}$
Base	2-Ethylhexyl Acrylate	-60	9.22
	Butyl Acrylate	-55	9.77
	Isooctyl Acrylate	-60	9.22
T_g modifing	Methyl Acrylate	10	10.56
	Ethyl Acrylate	-25	10.2
	Vinyl Acetate	30	10.56
	Methyl Methacrylate	105	9.93
Chemically Functional	Acylic Acid	110	14.04
	Methacrylic Acid	230	12.54
	Hydroxy Ethyl Acrylate	-15	13.5
Non-polar T_g Modifing	t-Butyl Acrylate	50	9.36
	t-Butyl Methacrylate	105	9.07
	Isobornyl Acrylate	96	9.71
	Isobornyl Methacrylate	155	9.5

Figure 3. Common acrylic monomer and their T_g’s and solubility parameters.

Designing an acrylic PSA with monomers that have lower solubility parameters will inherently enable the PSA to wet a wider variety of materials that can include various plastic substrates.

In “Viscoelastic Windows of Pressure Sensitive Adhesives”, E.P. Chang,[4] details a quadrant approach of classifying polymeric materials by loss and storage modulus measurements. This method utilizes mechanical analysis to predict the ability of a material to flow. It does not predict wetting because it does not include surface energy effects. However, using these techniques, general application quadrants can be identified by a materials flow properties as seen in Figure 4.

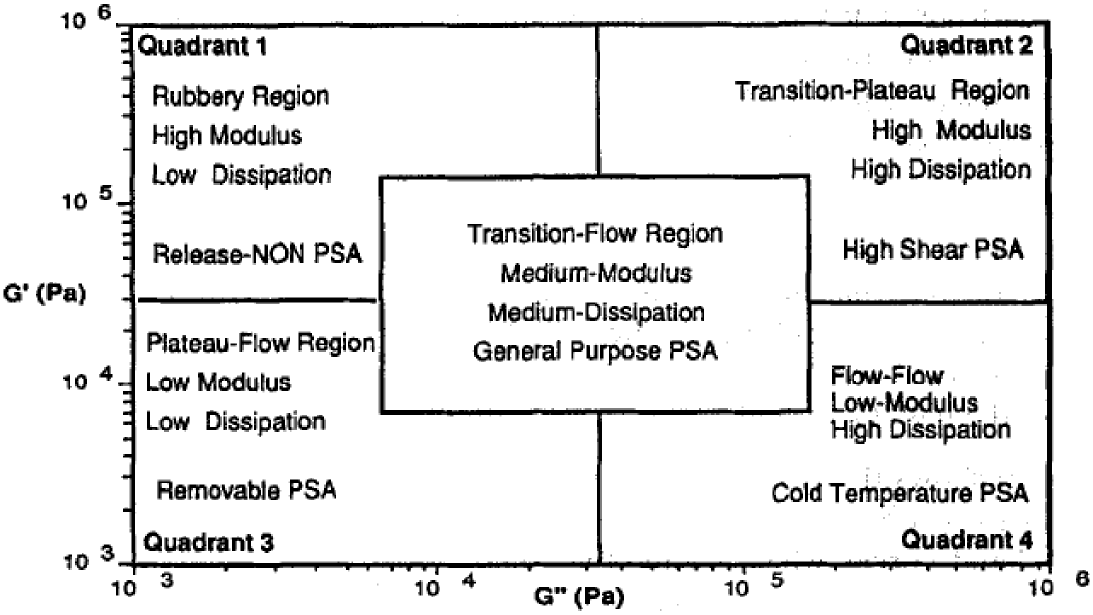

Figure 4. Chang’s quadrant approach to material classification.

From these quadrants pressure sensitive adhesives can be classified by their flow characteristic into types, which often translates into applicable market applications as seen in Figure 5. Quadrant 4, high G’’ low G’ materials or Type 1 PSA’s generally are high peel and low shear materials, that are usually high solids. These materials tend to be water based and are utilized in markets such as labels and graphics. Type 2, the central region of the viscoelastic window, is moderate to high peel and moderate shear materials. Type 2 PSA’s are utilized in some high performance label, vinyl graphic and medical applications. Quadrant 2 from the viscoelastic windows or Type 3 adhesive is moderate peel and high shear materials. Type 3 pressure sensitive adhesives can be used for high performance tape applications. Quadrant 3, or Type 4 materials include a broad range of removable or temporary adhesives used for protective films, and medical applications.

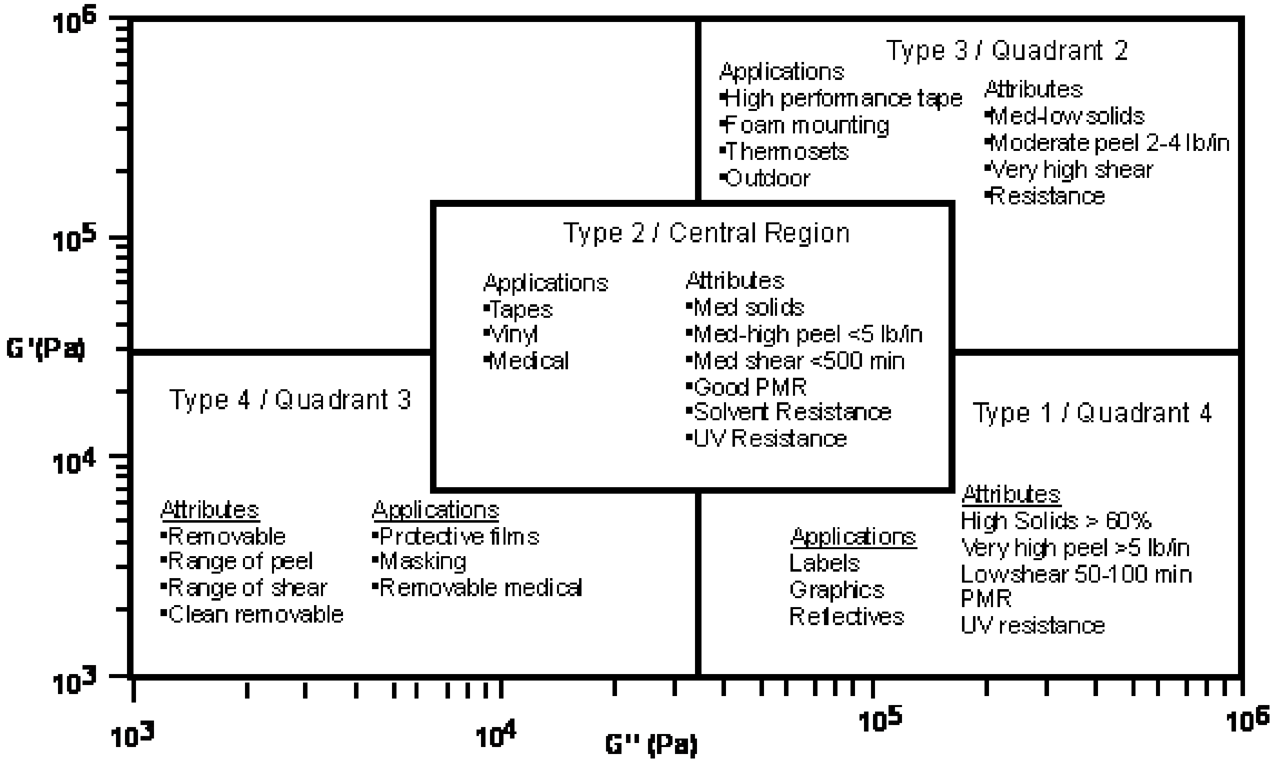

Figure 5. Adhesive quadrants classified as adhesive types

A tool used in designing an acrylic PSA of desired viscoelastic properties is to modify the glass transition of the material. Traditionally this is done by incorporation of high T_g modifying, or chemically functional monomers as shown previously in Figure 3 above. However incorporation of significant amounts of these monomers into an acrylic base polymer can raise the solubility parameter of the material such that it can no longer wet low surface energy substrates preventing an intimate bond. One traditional method of making an acrylic pressure sensitive adhesive chemically functional such that it can be chemically cross-linked is through the incorporation of acrylic acid. Acrylic acid has a low molar equivalency weight, has relatively high T_g, and can stiffen the acrylic base polymer because the acid functionality is very close to the main polymer chain. High molar equivalency weight acid functional acrylic monomer exist in the market, and these materials tend to be lower T_g, and do not stiffen the main acrylic base polymer as much as acrylic acid because the acid group is further removed from the backbone. Because the acid functionality on these materials are separated from the main chain by some chemical spacing group the acid functionality is better able to take part in hydrogen bonding with a substrate. Higher molar equivalency acid functional materials also result in an overall lower solubility parameter polymer because there are less acid groups than an acrylic acid containing system. These functional monomers are often the adducts of alcohol or amine functional (meth)acrylics and an anhydride, or ring opened cyclic compounds such as caprolactam.

Materials and Methods

Unless otherwise noted, the following test methods were used for evaluating the adhesive properties of the acrylic polymers.

PSA PERFORMANCE TEST METHODS

Test	Condition
180° Peel	a, b,
15 Minute Dwell	
24 Hour Dwell	
1 Week Dwell	
Williams Plasticity Index	c
Shear Strength	d
Shear Adhesion Failure Temp (SAFT)	e

(a) Peel, sample applied to a stainless steel panel with a 5 pound roller with 1 pass in each direction. Samples conditioned and tested at 23°C.

(b) Peel, sample applied to a high density polyethylene or polypropylene panel with a 5 pound roller with 5 passes in each direction. Samples conditioned and tested at 23°C.

(c) Williams Plasticity Index (WPI): A two gram spherical ball of dried adhesive is subjected to a compression test using a 2 Kg weight at 38.8ºC for 15 mins. Thickness of the sample after 15 mins is reported.

(c) Shear: 1 kg weight with a 1/2 inch by 1 inch overlap. Sample applied to a stainless steel panel with a 10 pound roller with 5 passes in each direction. Samples conditioned and tested at 23°C.

(d) SAFT: 1000 gram weight, 1 inch by 1 inch overlap (2.2 pounds/square inch). Sample applied to a stainless steel panel with a 10 pound roller with 5 passes in each direction. Samples conditioned for 1 hour at 23°C and 15 minutes at 40°C. Temperature increased by 0.5°C/min. until failure.

Two acrylic base polymers have been developed utilizing low solubility parameter T_g modifying and a high equivalency weight acid functional monomers. The new Type 2 and 3 polymers have a Tg of -45 and -35°C respectively as seen in Figure 6

	Monomers	Level (ppH)	Theoretical T_g (°C)
Type 2	Base Acrylic	80	-45
	T_g Modifier	10	
	Aliphatic Functional	10	
Type 3	Base Acrylic	70	-35
	T_g Modifier	20	
	Aliphatic Functional	10	

Figure 6. New Type 2 and 3 polymer designs.

The polymers were cast from solvent, cross-linked with aluminum acetyl acetonate, and compared to traditional commercially available Type 2 and 3 polymers that contain short chain polar T_g modifying monomers, and acrylic acid. All PSA testing was performed at a 50 g/m^2 coat weight using a polyethylene terephthalate (PET) face stock and test methods are in conformance with PSTC 101.

Results and Discussion

Figure 7 displays the 180° peel adhesion to stainless steel, 4.4lbs per square in static shear, and the williams plasticity index (WPI) of the traditional Type 2 and 3 compared to the LSE type 2 and 3 polymers.

Test	Traditional Type 2	Traditional Type 3	LSE Type 2	LSE Type 3
180º Peel to Stainless Steel 15 min dwell (Lbs/in)	3.70	4.50	3.44	4.23
180º Peel to Stainless Steel 24 hr dwell (Lbs/in)	4.23	4.76	4.38	4.81
180º Peel to Stainless Steel 1 week dwell (Lbs/in)	7.11 split	5.50	5.14	5.01
4.4 Lb/ Sq. in Static Shear (minutes)	617.7	9652.3	523.6	6251.2
William Plasticity Index (mm)	3.25	5.20	3.54	4.46

Figure 7. Peel adhesion to stainless steel, 4.4lbs/sq inch static shear, and WPI of the four polymers.

The properties of the new polymers are very comparable to the traditional acrylic PSA's when measured on stainless steel. However, when the adhesion to common olefin substrates like polypropylene and high density polyethylene are measured significant difference can be seen, as shown in Figure 8.

Test	Traditional Type 2	Traditional Type 3	LSE Type 2	LSE Type 3
180° Peel to Polypropylene 15 min dwell (Lbs/in)	0.56 zip	0.11 zip	1.68	2.68
180° Peel to Polypropylene 24 hr dwell (Lbs/in)	0.7 zip	0.28 zip	1.86	3.42
180° Peel to Polypropylene 1 week dwell (Lbs/in)	0.54 zip	0.37 zip	1.89	3.67
180° Peel to High Density Polyethylene 15 min dwell (Lbs/in)	0.41	0.48	1.37	1.45
180° Peel to High Density Polyethylene 24 hr dwell (Lbs/in)	0.50	0.41	1.51	1.56
180° Peel to High Density Polyethylene 1 week dwell (Lbs/in)	0.66	0.24	1.54	1.80
4.4 Lb/ Sq. in Static Shear (minutes)	617.7	9652.3	523.6	6251.2
William Plasticity Index (mm)	3.25	5.20	3.54	4.46

Figure 8. Peel adhesion to polypropylene, and high density polyethylene

Both the traditional Type 2 and 3 polymers exhibit low peel values and severe zipping or slip stick on polypropylene and smooth but low adhesion values on high density polyethylene compared to the new LSE compositions.

Tackification

An often utilized method of improving adhesion to low surface energy substrates is the addition of a tackifying resin. Tackifying resins are used to raise the Tg, lower the modulus and often lower the solubility parameter of an adhesive formulation. There are three main classes of tackifying resins. Hydrocarbon resins are based on petroleum feed stocks and are synthetically polymerized. Rosin and Terpene based resins are derived from natural feed stocks and then chemically modified. Rosin Ester tackifiers are one of the most commonly used tackifiers used in acrylic PSA’s. These materials are the product of esterification of crude rosin acid with glycerol or other common multi functional alcohol. Figure 9 displays the adhesion performance on Polypropylene and Stainless Steel of a 20pph addition of an 85ºC softening point rosin ester to the base polymers mentioned above.

Test	Rosin Tackified Traditional Type 2	Rosin Tackified Traditional Type 3	Rosin Tackified LSE Type 2	Rosin Tackified LSE Type 3
180º Peel to Polypropylene 15 min dwell (Lbs/in)	7.45 split	0.58 zip	3.20	3.91
180º Peel to Polypropylene 24 hr dwell (Lbs/in)	7.63 split	0.59 zip	3.58	4.35
180º Peel to Polypropylene 1 week dwell (Lbs/in)	7.3 split	0.73 zip	3.47	4.68
180º Peel to Stainless Steel 1 week dwell (Lbs/in)	7.67 split	6.32	5.87	5.84
4.4 Lb/ Sq. in Static Shear (minutes)	374.2	9563.2	529.6	6687.5
William Plasticity Index (mm)	2.85	4.22	3.40	3.65

Figure 9. Adhesive performance for 20pph loading addition of rosin ester tackifier.

The rosin ester tackifier enabled the traditional Type 2 polymer to adhere well to polypropylene, although the traditional Type 3 polymer still exhibited zipping and low adhesion with rosin ester addition. Both LSE polymers exhibited the expected increase in peel one would expect with tackifier addition as well as maintaining high shear performance.

Terpene resins are produced by oligomerization of pinene and limonene to produce low molecular weight high softening point non-polar tackifiers. Terpene resins are not commonly used in acrylic pressure sensitive adhesives because traditionally they have very limited solubility in acrylics containing polar monomers. However, when low solubility acrylic monomers are used to design an acrylic pressure sensitive adhesive like those of the LSE Type 2 and 3 mentioned above these non-polar tackifers become useful. Figure 10 displays the adhesive performance of a 105ºC softening point polyterpene resin addition at a 20pph loading level to the four polymers above.

Test	Terpene Tackified Traditional Type 2	TerpeneTackified Traditional Type 3	Terpene Tackified LSE Type 2	Terpene Tackified LSE Type 3
180º Peel to Polypropylene 15 min dwell (Lbs/in)	3.18	1.4 zip	4.70	5.23
180º Peel to Polypropylene 24 hr dwell (Lbs/in)	3.32	2.03 zip	4.68	5.31
180º Peel to Polypropylene 1 week dwell (Lbs/in)	3.27	2.06 zip	4.62	5.42
180º Peel to High Density Polyethylene 15 min dwell (Lbs/in)	1.87	0.54 zip	2.86	3.22
180º Peel to High Density Polyethylene 24 hr dwell (Lbs/in)	2.00	1.03 zip	3.06	3.41
180º Peel to High Density Polyethylene 1 week dwell (Lbs/in)	2.05	1.02 zip	3.24	3.35
180º Peel to Stainless Steel 1 week dwell (Lbs/in)	6.90	4.62	9.42	7.98
4.4 Lb/ Sq. in Static Shear (minutes)	2147.3	10000+	2568.5	6685.2
William Plasticity Index (mm)	3.57	5.11	3.59	3.62

Figure 10. Adhesion data for 20pph terpene addition

The terpene addition to the LSE type polymers results in a good broad based adhesive to low and high surface energy substrates, and excellent shear. The terpene resin however results in slight improvement in the case of the traditional type 2 and zipping failures when added to the traditional type 3.

In addition to enhanced adhesion to low surface energy substrates the LSE compositions and the terpene tackified materials offer increased thermal stability over traditional rosin ester containing acrylic pressure sensitive adhesives. Thermal aging of several adhesive constructions was performed at 120ºC on Propylene test panels. Adhesion was measured prior to thermal exposure, and every week for four weeks. Figure 11 displays the peel adhesion measured at each interval for a commercially available high strength adhesive, a rosin ester containing acrylic, and all acrylic low solubility parameter composition, and a terpene tackified low solubility parameter acrylic.

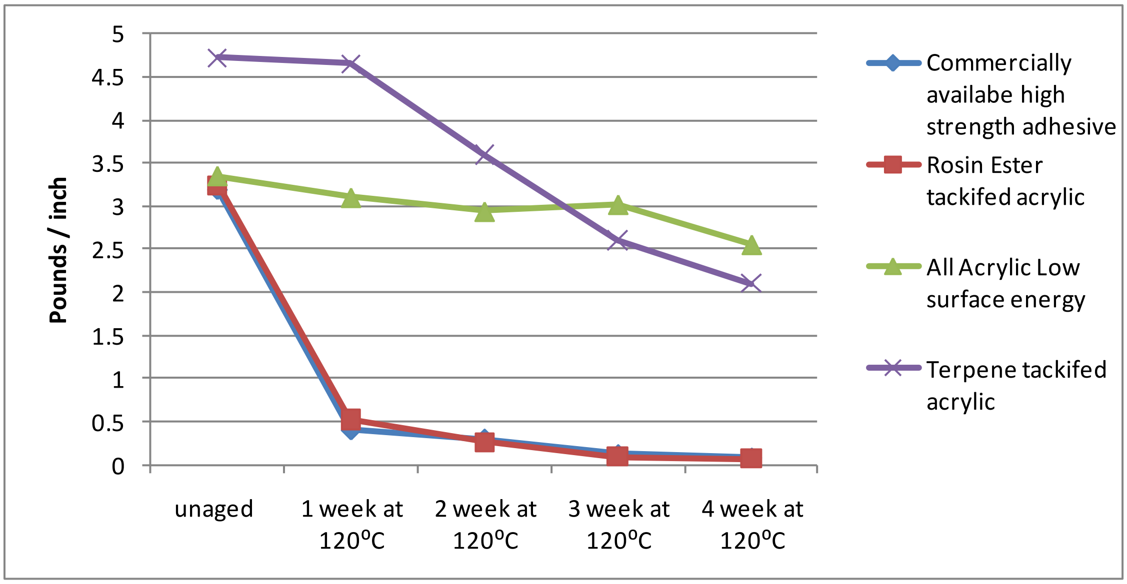

Figure 11. Peel adhesion as a function of thermal aging time

The rosin ester containing acrylic and the commercially available high strength adhesive saw a dramatic decrease in adhesion upon thermal exposure. However the all acrylic composition retained virtually all its adhesion through 4 weeks of aging. The terpene containing sample lost about 50% of its peel force over the 4 week aging period, which is still superior to that of the control. This decrease in peel exhibited by the tackified materials is likely caused by residual unsaturation being oxidized in the tackifiers. The rosin ester used in this study is hydrogenated, but hydrogenation is never driven to 100% conversion. The terpene materials are inherently more saturated than the rosin based tackifiers, but do still contain some unsaturations. However the terpene tackified material does offer a thermal stability improvement over rosin ester containing adhesives.

Inter Penetrating Networks

Polyacrylate polyether inter penetrating networks (IPN) have been previously disclosed.[5] These materials combine the elastomeric, high modulus and flexibility of a sealant with the wetting, and viscoelastic characteristic of a pressure sensitive adhesive to produce a hybrid IPN high performance pressure sensitive material. One class of reactive oligomer that can be used to make the IPN materials is a silane functional telechelic Polypropylene oxide available from various suppliers. The combination of the Polypropylene oxide oligomer, which has a very low solubility parameter, with the low solubility parameter acrylic polymers previously discussed allows for the production of high performance adhesives that adhere very well to olefin substrates. The adhesive performance of an IPN made using the Type 3 LSE acrylic discussed above, a propylene oxide oligmer, and a terpene resin can be seen in Figure 12 compared to the terpene tackified Type 3 LSE polymer, and a commercially available high strength LSE adhesive.

Test	High Strength LSE Adhesive	Terpene Tackified Type 3 LSE Acrylic	LSE Acrylic IPN
180º Peel to PolyPropylene 15 min dwell (Lbs/in)	3.79	4.48	4.62
180º Peel to PolyPropylene 24 hr dwell (Lbs/in)	5.10	4.77	5.21
180º Peel to PolyPropylene 1 week dwell (Lbs/in)	5.26	4.67	5.35
180º Peel to Stainless Steel 1 week dwell (Lbs/in)	5.36	5.42	6.32
4.4 Lb/ Sq. in Static Shear (minutes)	10000.0	6685.2	10000.0
William Plasticity Index (mm)	NA	3.6	4.7
SAFT (degrees C)	200.0	200.0	200.0

Figure 12. Adhesive performance of the LSE IPN material compared to the terpene tackified type 3 polymer and a high strength commercially available adhesive.

The IPN material exhibits enhanced peel and shear properties over the terpene tackified base polymer alone. It also displays significantly higher williams plasticity index indicating that the IPN material will slit and convert much easier. The enhancement in peel, shear and WPI suggests some synergistic effects of the polyacrylate polyether IPN system.

Conclusions

The expanding use of light weight low surface energy plastic materials in many common applications requiring pressure sensitive adhesive has created the need for materials that can bond well to these new substrates. Acrylic pressure sensitive adhesives exhibiting enhanced adhesion to these low surface energy plastics have been demonstrated. Common formulation additives such as tackifiers can be utilized; in addition low solubility parameter tackifying resins such as polyterpene resins have shown applicability with these new acrylic pressure sensitive adhesives. These all acrylic, and terpene tackified pressure sensitive materials also offer enhanced thermal stability over traditional rosin containing adhesives. Finally, IPN’s made with these low solubility parameter acrylics enable the production of a high performance hybrid pressure sensitive adhesive.

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