Recent Progress in UV/EB-Curable Pressure Sensitive Adhesives

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Abstract

Energy-curable pressure sensitive adhesives (EC-PSAs) eliminate the need for drying, solvent extraction, or preheating steps (compared to traditional water-borne, solvent-borne, and hot melt methods). These processing benefits make such adhesives particularly suitable for temperature-sensitive substrates and in-line application. Here, we demonstrate structure-property relationships between PSA formulation and properties such as tack, peel strength, shear resistance, and temperature performance. Highlights include screening the viscoelastic properties and investigating routes to higher shear adhesion failure temperature (SAFT) PSAs.

Introduction

Adhesives are nonmetallic materials used to bond other materials, by adhesion to their surfaces and cohesion within the adhesive layer. Two different processes exist which describe most adhesive bonding: 1) the adhesion phenomenon or 2) by PSA action. In the former, adhesive fluid is transformed into a solid upon bonding. A PSA, however, conserves its fluid state after its bond building. Therefore, some notable benefits of PSAs are that i) the resistance to de-bonding is moderate and ii) the joint may be delaminated without destroying the laminate components.[1]

Today, the three main PSA technologies are water-borne (WB-PSA), solvent-borne (SB-PSA), and hot melts (HM-PSA). The global demand for these types of PSAs total ~ 93% with the rest being UV-curable hot melts (UVHM-PSA) and silicone-based PSAs.[2] Broadly speaking, SB-PSAs and UVHM-PSAs tend to offer 'high' performance with HM-PSAs offering medium performance while WB-PSA offer lower performance at the lowest cost. Each of these technologies has its advantages but also, distinct disadvantages, e.g., low solvent/plasticizer resistance for HM-PSAs, high concentration of volatile organic compounds (VOC) for SB-PSAs, and large equipment footprints required for WB-PSAs.

Herein, we present a UV curable or electron beam (EB) curable PSA made from 100% solids, i.e., no solvents. These energy-curable systems are sometimes referred to as EC-PSA 'syrup' formulations. The product can be applied as a viscous liquid system without the need for heat (depending on the viscosity requirements of the coating unit). Without solvents or water, this product eliminates the need for highly-regulated solvent extraction systems or the need for time-consuming oven drying steps. As a result, EC-PSAs can lead to higher productivity and lower manufacturing costs vs conventional PSA products. Additionally, rapid cure, improved dimension accuracy, heat resistance, chemical resistance, and heavy coating weights are possible. To use EC-PSAs, existing lines can be retrofitted with a UV lamp, a UV-LED lamp, or an EB unit. Additionally, EC-PSA syrups provide ideal formulation platforms for cure-in-place (CIP) automated applications. As will be discussed below, the viscosity of the EC-PSA formulation can be adjusted

by varying the ratio of components, thus tailoring the formulation for use in any deposition system. More so, this approach allows for control over the performance of the PSA through choice and composition of starting ingredients.

The main components in a typical EC-PSA formulation are:

- Oligomers: Provide much of the shear strength and also affect tack, peel, reactivity, creep resistance, heat resistance, and chemical resistance.
- Monomers: Mainly serve as reactive diluents, i.e., lower the viscosity of the formulation. These components also control surface wetting, leveling, and other physical properties.
- Photo-initiators: Absorb UV-light to produce free radicals that induce polymerization. Formulations intended for EB curing to do not need photo-initiators to polymerize.
- Additives
  - Stabilizers prevent premature curing due to low-level light exposure in storage.
  - Tackifiers improve the pressure-sensitive nature or "stickiness" of the adhesive.
  - Other additives include: adhesion promoters, fillers, antioxidants, plasticizers, color pigments, dyes, defoamers, flatting agents, wetting agents, and slip aids.

In general, the most fundamental material properties governing EC-PSA performance are[3]:

- Rheology
  - Study of the change in form and flow of a material. It is generally applied to viscoelastic materials.
  - Uncured state: rheology is important with regard to application and coating.
  - Cured state: PSA material must have sufficient flow to provide wetting and tack, yet have enough resistance to stress to provide for high adhesive strength.
- Molecular Weight
  - PSAs are based on very high-molecular-weight rubber polymers, which restrict flow by molecular entanglement.
  - When high strength, heat resistance, and chemical resistance are required, the molecules must be chemically crosslinked to provide for a three-dimensional network structure.
- Acrylate Functionality
  - Number of unsaturated sites per molecule.
  - Crosslink density increases with the functionality of the resin, all else equal.

Additionally, the type of substrate is critical to EC-PSA performance. In general, metals have high surface energy and tend to result in high peel strengths while plastics have low surface energy and tend to result in lower peel strengths. For plastics, treated surfaces tend to improve PSA performance (versus untreated surfaces).

Experimental details

Sample Preparation: PSAs were typically coated onto a 2 mil untreated PET facestock using an automatic film coater (MTI Corp MSK-AFA-II). The thickness of the liquid PSA coating was controlled by a combination of the viscosity of the formulation, the gap of the coater (adjusted by a micrometer screw gauge), and the speed of the automatic coater. The liquid PSA coating was then cured by using one or multiple passes under one or two 400 W/in mercury vapor lamps (Inpro system) with a speed of 50 ft/min. The energy dose (mJ/cm^2) was measured using a power puck (EIT UV Powerpuck II). The PSAs were also cured using UV-LED lamps (365nm or 395nm). After curing, the samples were laminated onto silicone release paper and 1" strips were cut for testing. For EB curing, the liquid PSA coatings were cured using an ESI Ebeam unit at 50 ft/min, typically between 5-15 Mrad and 175 kV with just one pass.

180° Peel Strength: The PSA peel samples were prepared by applying 1"-wide PSA strips to stainless steel or polypropylene panels (ChemInstruments) using two passes with a 4.5 pound automatic roller. The PSA-laminated samples and panels were stored in a constant humidity room (at 72°F and 60% humidity) for a predetermined dwell time (1 hour, 1 day, or 3 days) before testing. The peel strengths were measured at a 180° angle with a peel speed of 12 in/min following the ASTM-D903-98 standard using a tensile tester (Instron 5543).

Probe Tack: The probe tack was measured following ASTM-D2979-95 using a probe tack tester (ChemInstruments PT-500).

Shear Resistance: Shear resistance was tested following ASTM 4498-95. One square inch of PSA was applied to a stainless steel panel using two passes with a 4.5 lb automatic roller. The PSA and panel were allowed a dwell time of 1 hour before testing. A mass of 1 kg or 2 Kg was then attached to the other end of the PSA strip. A shear tester (ChemInstruments Shear-10) was used to hold the samples vertically while the mass suspended and to record the time required for the PSA strip to fully detach from the substrate. The shear resistance is reported as this time in minutes.

Shear Adhesion Failure Temperature (SAFT): SAFT test samples were prepared in a similar manner to shear resistance samples. One square inch of PSA was applied to a stainless steel panel using two passes with a 4.5 lb automatic roller. The PSA and panel were allowed a dwell time of 1 hour before testing. A 1 kg mass was then attached to the other end of the PSA strip. A shear tester housed in an oven was used to perform the test. The starting temperature (T_0) was noted (usually room temperature) and the oven temperature ramp (ramp rate of 1 °C/min) and timer were started simultaneously. When the mass fell, the SAFT value for that PSA sample was calculated as: ramp rate (°C/min) x time (min) + T_0 (°C).

Rheology: Dynamic mechanical analysis experiments were performed using a rheometer (TA Instruments RDA111) at a frequency of 1 Hz and heating rate of 3 °C/min. All samples were tested using 8 mm parallel plate applying a static compressive force and tested in shear mode in the linear viscoelastic region. The peak tan δ temperature and storage modulus G' at 20 °C are reported. Frequency sweeps were done at 30 °C in RDA 111, using 8 mm parallel plates from 0.01 rad/s to 100 rad/s.

Results & Discussion

In this paper, we investigated the role of oligomers, monomers, photo-initiators and curing on EC-PSA performance.

Choice of Oligomers: Previously, we described how rheology can be used to down-select oligomers for use in PSAs.[4] Here, the Dahlquist Criterion specifies that for measurable quick tack, the elastic modulus must be below a certain fixed value which is fairly independent of the nature of the adhesive, the adherend, and the applied pressure. In the case of PSAs, tack ceased when the storage modulus (G') was greater than 10^5 Pa.[5,6] A typical DMA screening of four commercially available oligomers is shown in Fig. 1. Here, Oligomers 1 and 2 would not be suitable for use in PSAs because G' is greater than 10^5 Pa. Oligomers 3 and 4 both meet the Dahlquist Criterion for PSAs. Oligomer 3, however, would be most suitable because of its ability to flow while maintaining some structural integrity.

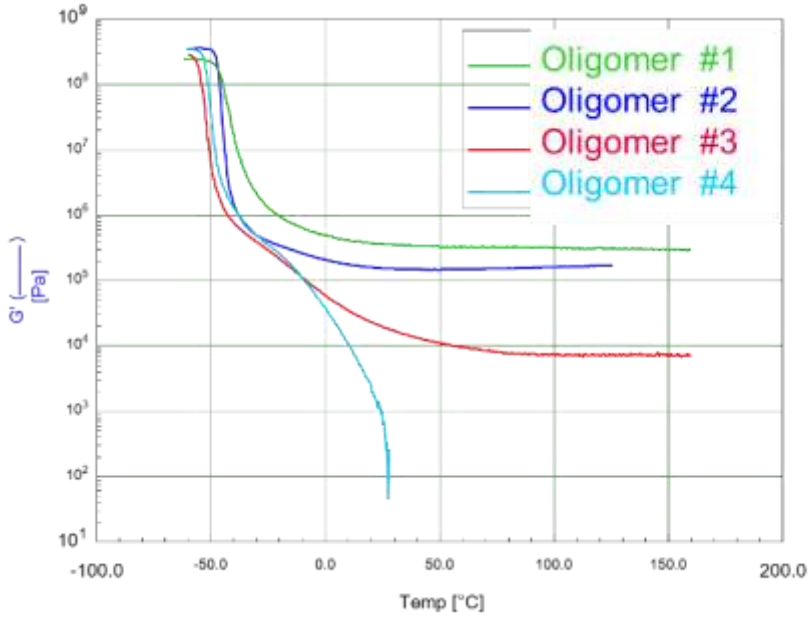

Figure 1: Storage modulus (G') as a function of temperature for four commercially available Sartomer oligomers.

Choice of Monomers: The coating unit used in the PSA application often sets the viscosity limits of the liquid formulation. This constraint in turn dictates the amount of monomer(s) that go into the final EC-PSA formulation. Many monomers have viscosities as low as 10 cP. The choice of acrylate monomer depends on the final PSA performance being sought, i.e., type of substrate, peel strength, shear, tack, application temperature of liquid PSA, service temperature of cured PSA, removable/permanent use, etc. In general, increasing the monomer functionality leads to higher cure speed, higher T_g, higher crosslink density, higher shear strength, greater chemical

resistance, greater thermal resistance, and lower flexibility. Often a combination of monomers of varying T_g is used to tailor properties.

Certain trends were observed for the EC-PSA in its cured state. When the adhesive T_g was greater than the service temperature, the PSAs were rigid and to some extent brittle, had high shear resistance, low impact and peel strengths, high temperature resistance, high barrier properties against chemicals and water, poor resistance to thermal cycling, low water uptake and swelling, were prone to crack propagation, and had low thermal expansion coefficients. Conversely, the opposite effects were observed when the T_g of the EC-PSA was less than service temperature.

Choice of Photo-initiator: To investigate the effects of photo-initiator concentration in an EC-PSA formulation, we varied the diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) loading from 1-5% into a base UV PSA formulation (PRO 13733). The liquid formulation was cured at 200 mJ/cm^2 (low cure, LC) and 400 mJ/cm^2 (high cure, HC). The thickness of the cured PSA was held constant at 2.7 mils. Fig. 2 shows the results of the PSA performance evaluation that followed. The testing included peel strength on stainless steel and polypropylene at different dwell times, and shear resistance using a 2 kg mass. At 1% TPO concentration, we observed some adhesive performance but no shear resistance: most probably an indication that the formulation was under-cured. We noticed that the shear resistance increased from ~500mins to ~ 2000 mins for formulations made with 3% TPO and 5% TPO respectively. Not surprisingly, we expect that this is due to greater degree of cure for 3% TPO vs 5% TPO. The effect of photo-initiator concentration on peel strength is less evident as other factors such as dwell time, energy dosage and thickness play larger role. However, overall better performance was seen with 5% TPO vs 3% TPO.

	1% TPO		**3% TPO**		**5% TPO**	
	LC	HC	LC	HC	LC	HC
Peel strength on stainless steel (lb/in)						
1 day	1.00	1.25	4.99	5.61	5.79	7.68
3 day	0.36	1.10	8.47	3.92	7.42	7.57
Peel strength on polypropylene (lb/in)						
1 day	0.90	1.10	4.16	4.63	4.33	4.85
3 day	1.12	0.35	4.23	3.60	6.27	6.2
Shear resistance on stainless steel, 2 kg (mins)						
1 hour	0	0	378	536	2,276	2,062
(UV-PSA thickness = 2.7 mil)	LC = 200 mJ/cm^2			HC = 400 mJ/cm^2		

Figure 2: Effect of photo-initiator concentration on PSA performance.

We also investigated the choice of photo-initiator on PSA performance. Here, we investigated PSA performance of a base UV PSA formulation (PRO 13733) with 5% loading of either 2,4,6-trimethylbenzoyl-diphenyl phosphine oxide (TPO), Omnirad® 184, Omnirad® 2022 or Omnirad® 4265 and with 3% loading of phenylbis 2,4,6-trimethyl benzoyl-phosphine oxide (BAPO) (to standardize amount of radicals generated). PSA performance for formulations with these different photo-initiators are captured in Fig. 4 (PSA adhesives were all 2.7 mil thick and cured using H-bulb at 400 mJ/cm^2). The results indicate that the choice of photo-initiator is crucial to PSA performance and is dependent on the other components in the formulation and on curing conditions.

	Photoinitiator				
	BAPO	TPO	Omnirad 184	Omnirad 2022	Omnirad 4265
Peel strength on stainless steel (lb/in)					
1 day	3.92	7.68	5.21	4.26	2.92
3 day	5.13	7.57	9.00	4.78	4.38
Peel strength on polypropylene (lb/in)					
1 day	4.10	4.85	3.68	3.51	3.23
3 day	5.10	6.20	4.78	3.97	3.45
Shear resistance on stainless steel, 2 kg (mins)					
1 hour	692	2,062	880	1,524	1,200

Figure 3: Effect of photo-initiator type on PSA performance.

UV PSA vs EB PSA: We investigated the PSA performance of a base energy curable formulation (PRO 13733) cured via UV and EB (Fig. 4). For the UV-curable formulation, 5% TPO was employed while no photo-initiator was required for EB curing. Just as different adhesive properties can be accessed within UV curing alone, different PSA performances were observed between the two curing methods. The main advantage of EB curing was higher shear and unprecedented high SAFT. We have also seen high PSA performance when curing using UV-LED lamps (365 nm and 395 nm) comparable to that shown in Fig. 4, but this finding has not been fully investigated.

Property	UV cured	EB cured
Viscosity at 25°C (cP)	6,650	6,650
Cured PSA Thickness (mil)	2.7	2.1
Curing Method	UV (H Bulb)	EB
Energy (J/cm^2)	0.49	10 Mrad/175 kV
180° Peel on Stainless Steel; 1 day (lb/in)	7.6	4.2
180° Peel on Polypropylene; 1 day (lb/in)	4.8	4.5
Probe Tack (lb)	2.26	2.06
Room Temp Shear 2 kg (hr)	34	>167
Room Temp Shear 1 kg (hr)	84	>167
SAFT (^0F)	185	435
Refractive Index	1.49	1.49

Figure 4: PSA performance comparison for UV cured and EB cured PSAs.

Versatility of EC-PSAs

Fig. 5 captures the range of PSA performance (tack and peel) achievable to-date via UV curing. While this graph does not capture the viscosity of each data point, it does demonstrate how EC-PSAs can be tailored to meet very specific PSA application targets. One interesting advantage that EC-PSAs may be able to offer is low tack with high peel strength, which could potentially be useful for applications where minimal pressure is required for bonding. Furthermore, Fig. 6 shows the range of SAFT values that can be achieved by either UV or EB. SAFT valves of > 400 °C is unprecedented and current R&D efforts are focused on extending the achievable property spaces of both UV- and EB-PSAs, e.g., UV-PSAs with high SAFT and high peel strength.

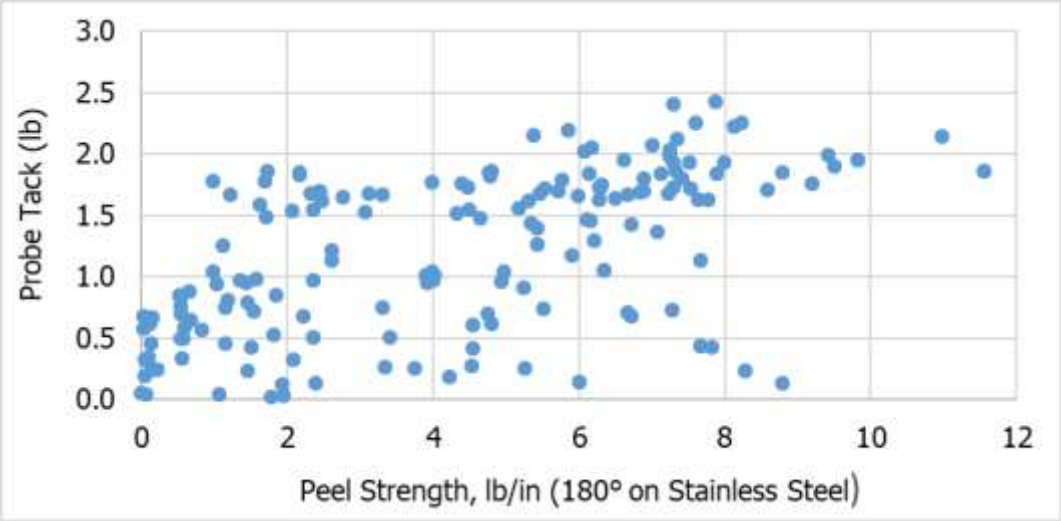

Figure 5: Range of UV PSA performance (tack and peel) achievable to-date.

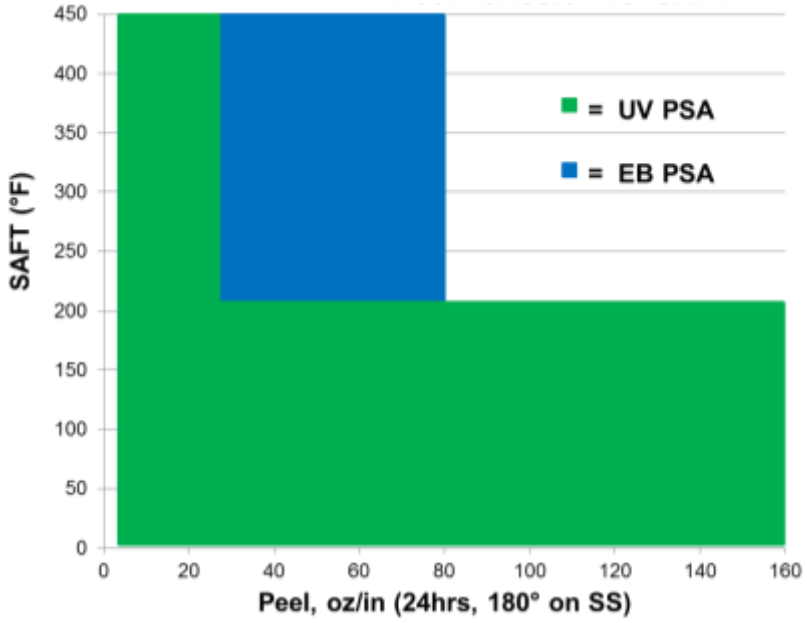

Figure 6: Overview of the achievable SAFT values as a function of peel strength for UV-PSAs and EB-PSAs.

Conclusion

In summary, we found that a number of variables affect EC-PSA properties, including rheology and chemical characteristics. The relationships between different measures of adhesive performance were analyzed, as were different methods of curing PSAs. Specifically, the choice and amount of oligomer, monomer, photo-initiator, and additives are all crucial to the starting-point liquid formulation. With this wealth of available chemistry, the range of achievable EC-PSA performance is quite broad and the ability to tailor each formulation to specific performance targets makes this approach very versatile.

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