Radiation Curable Pressure Sensitive Adhesives

Jin Lu and Chuck Dong
Arkema Inc., Sartomer Business Unit
Exton, PA 19341

Abstract

Pressure sensitive adhesives (PSA) are widely used in a variety of applications in forms of tapes, labels or graphics. They continue finding new applications in ever growing automobile, packaging and medical industries. Radiation curable syrup PSAs show advantages over the traditional technologies, such as solventborne, waterborne, and hotmelt PSA, in terms of productivity, environmental friendliness, cost efficiency and performance. The driving force behind the development of radiation curable syrup PSA technology is to reduce the volatile organic compound (VOC) emissions from solvent-based PSA systems, yet maintain the high performance of solventborne PSAs, which other technologies cannot achieve. This presentation focuses on the development of UV-curable syrup PSA products for high performance applications. These systems showed excellent peel strength and tackiness on both high surface energy stainless steel and low surface energy polypropylene. Extensive research work has been done to investigate the rheological properties of PSA to gain a deeper understanding of potential applications of these new products.

Introduction

A pressure sensitive adhesives is an adhesive which forms a bond when pressure is applied to bond the adhesive with the adherend. Pressure sensitive adhesives are generally based on acrylic, styrenic block copolymers or urethane chemistry, which have certain drawbacks during processing and film-forming. Acrylic based PSA systems are usually hot-melt type adhesive systems, solvent-based adhesive systems or water-based adhesive systems that facilitate a coating process. Due to the regulations on VOC emission, solventborne PSAs has been gradually replaced by hot melt or waterborne pressure sensitive adhesives. However, for the industrial specialty tape applications, solventborne technology is still the dominating technology. The main reason is that hotmelt or waterborne PSAs cannot deliver the high performance including high peel strength, high tack in combination of high shear. With the more stringent regulations on VOC, there is an urgent market need for a new technology to replace solventborne systems for such specialty applications.

During the last two years, Sartomer designed and developed a series of innovative formulated products to provide a solution to this market need~~s~~. In this paper, we demonstrate that 100% solids radiation curable syrup system can deliver the high performance that industrial specialty tape requires. The key benefits of this technology include, but not limited to:

- 100% solids without VOC
- High productivity
- No heat required during converting process
- High performance on both high surface energy substrates and low surface energy substrates

Experimental

Radiation curable syrup PSAs were developed based on specially designed oligomers and by comprehensive formulations. The viscosity of formulated adhesives are in the range of 5000 cps to 20,000 cps.

Sample Preparation

The pressure sensitive adhesives were drawdown onto the surface of 2 mil untreated PET film. The adhesives were cured under 400 W/in mercury vapor lamp at about 1 J/cm^2 curing energy. Afterwards, the samples were laminated onto a release paper. One-inch strips were cut for testing.

180° Peel Strength

The samples were prepared by applying one inch PSA strip to stainless steel or polypropylene panels using a 4.5 pound automatic roller. The laminated samples were dwelled at 72°F and 50% humidity for 3 days before testing. The peel strength was measured at 180° angle at a speed of 12 in/min following ASTM-D903-98 standard.

Probe Tack

The probe tack was measured following ASTM-D2979-95 using Probe Tack Tester PT-500 from ChemInstruments.

Shear Resistance

Shear resistance was tested following ASTM 4498-95. One square inch of adhesive samples was applied to the stainless steel panels and dwell for 1 hour before testing. Weight of either 1kg or 2kg was used, and the time was recorded.

Rheology Property

Dynamic mechanical analysis experiments were done on TA Instruments RDA111 rheometer at a frequency of 1Hz and heating rate of 3 C/min. All samples were tested using 8mm 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 sweep were done at 30C in RDA 111 , using 8mm parallelplates from 0.01 rad/s to 100rad/s

Results and Discussions

Rheology of several commercial oligomers was studied. It is found that the storage modulus at room temperature and tan δ of these oligomers are relatively high for PSA application. This requires significant formulation work to achieve the high performance. Several new oligomers were designed and synthesized to lower the storage modulus at room temperature and tan δ. New Oligomer 1 lower the storage modulus close to 10^5 Pa at plateau and stable up to 150°C, which can be easily formulated to PSA. The storage modulus of new oligomer 2 is lower than 10^4 Pa, which indicates this oligomer can form a soft but elastic film having cohesive strength up to 150°C. The oligomer itself can function as PSA. As comparison, the storage modulus of new oligomer 3 does not show a rubbery plateau region on temperature sweep indicating that this oligomer cannot be cured to an elastic film. The storage modulus of new oligomer 4 is similar to commercial product #2.

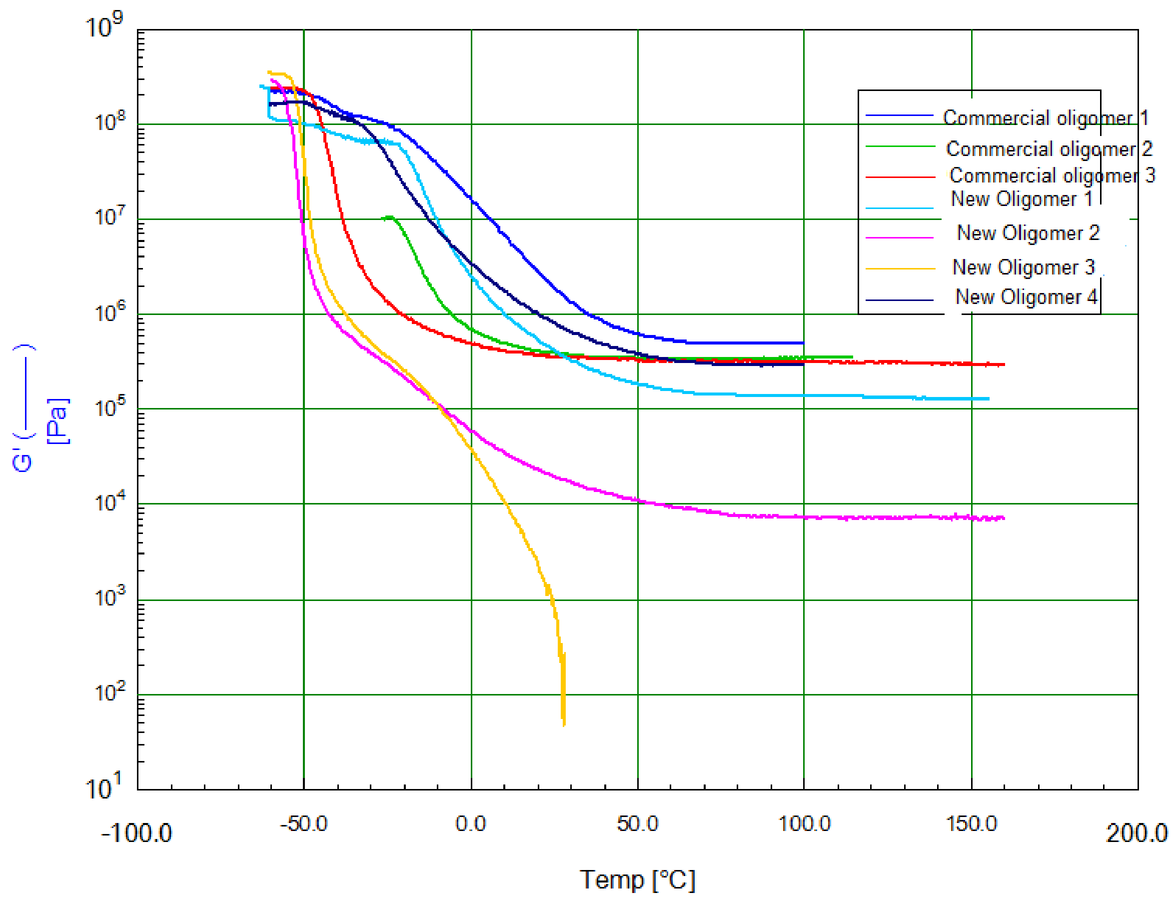

Figure 1. The temperature dependence of storage modulus (G') of oligomers.

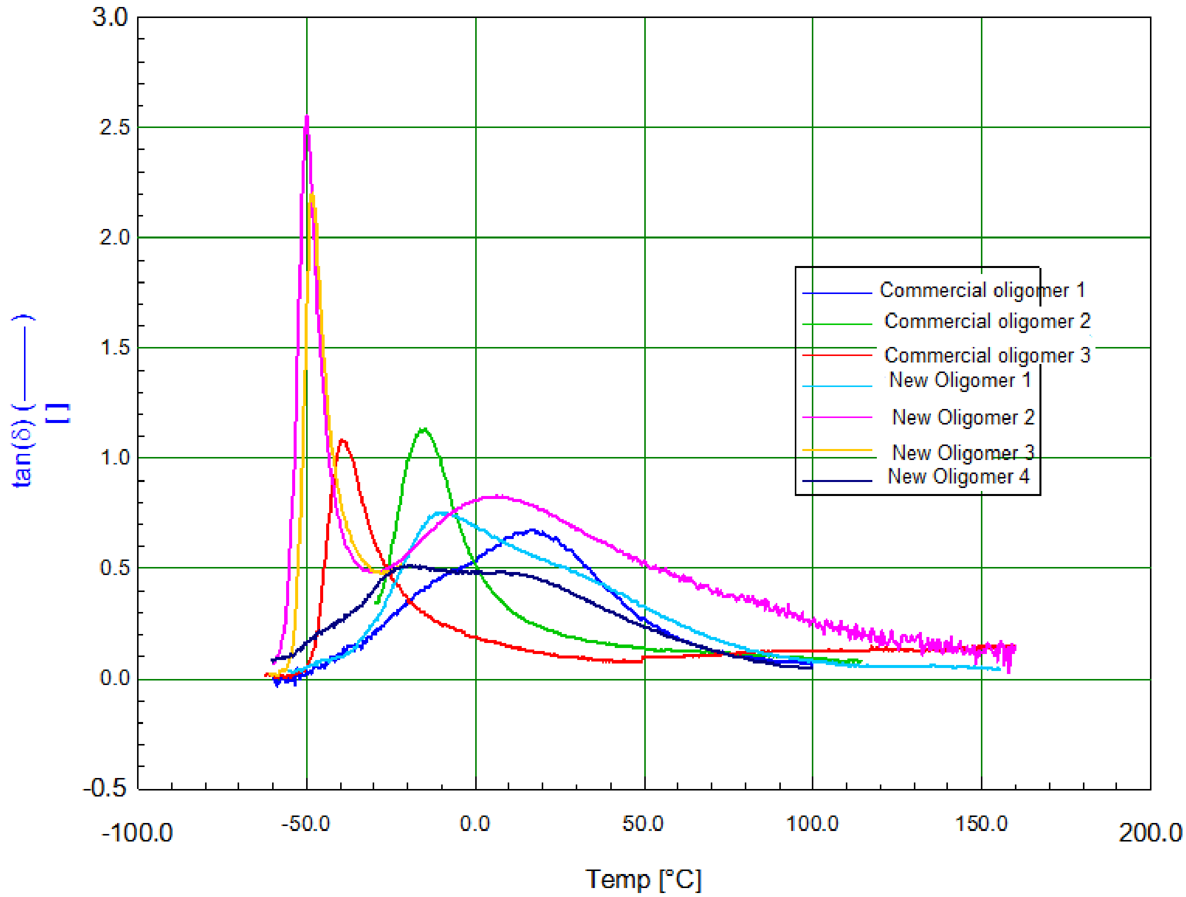

Figure 2. The temperature dependence of Tan (δ).

Comprehensive formulations were designed and tested based on new oligomers 1 and 2. A series of high performance UV curable PSA new products were developed. These 100% solids, UV curable syrup products have viscosity from 2000 cps to 20,000cps at room temperature, which enable the converting process without heat. Due to the correlation of viscoelastic properties of pressure sensitive adhesives (PSAs) with industry standard performance[1], the viscoelastic properties of cured PSAs were used as screening tools for this high performance PSA development. The typical viscoelastic properties of these high peel strength and high tack UV PSA syrup systems are presented in Figure 3. Two examples UV PSA 1 and UV PSA 2 are given. Based on Dahlquist contact criterion [2], tack did not occur when storage modulus was greater than 10^5 Pa. This theory was evidenced by our data. The UV PSAs offering excellent tack properties at room temperature does have storage modulus lower than 10^5 Pa. Table 1 presents the PSA performance of two examples. Figure 3 presents their rheology properties. UV PSA 2 has lower storage modulus and lower Tg compared to UV PSA 1, which enables better wetting the substrates, showing higher tack and peel adhesions. The viscoelastic windows of these two UV PSAs show that both of them are in quardrant 2 and central area corresponding to comparatively high/medium modulus (G') and high/medium dissipation (G") within the application rates (i.e. between 10^{-2} and 10^2 sec^{-1}). In general, this implies the higher shear performance.

Table 1. Pressure sensitive adhesives performance of UV PSAs.

	Probe Tack (lb)	Peel Strength (lb/in), Stainless Steel	Peel Strength (lb/in), Polypropylene
UV PSA 1	1.44	5.45	5.27
UV PSA 2	2.00	6.05	6.14

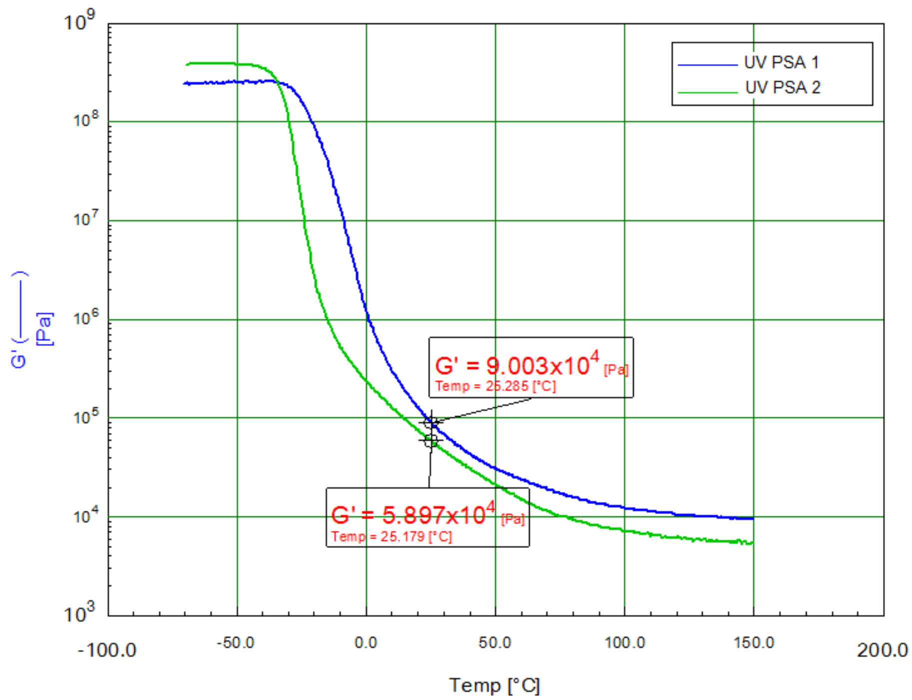

Figure 3 (a) The temperature dependence of storage modulus (G') of UV PSA 1 and UV PSA 2.

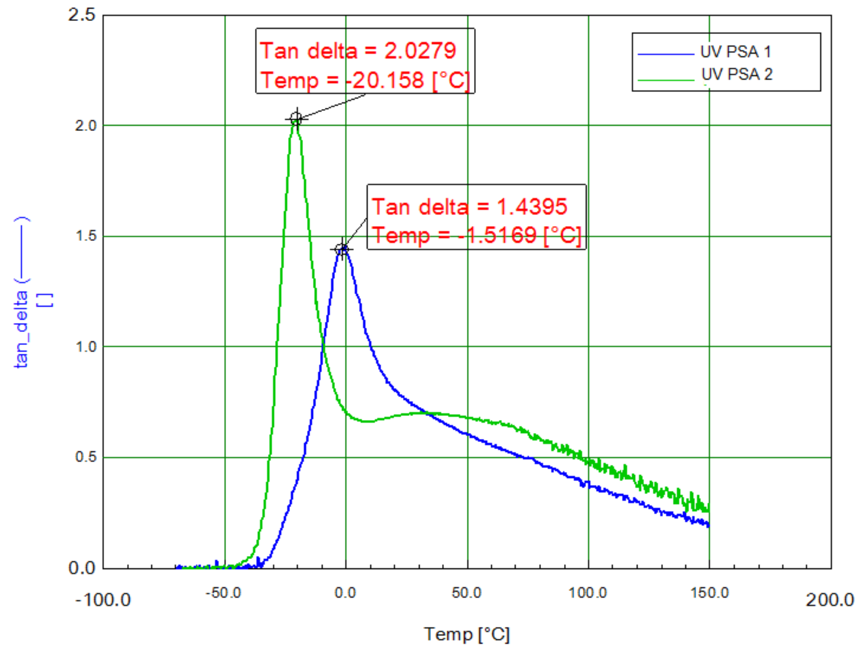

Figure 3 (b) The temperature dependence of Tan (δ) of UV PSA 1 and UV PSA 2.

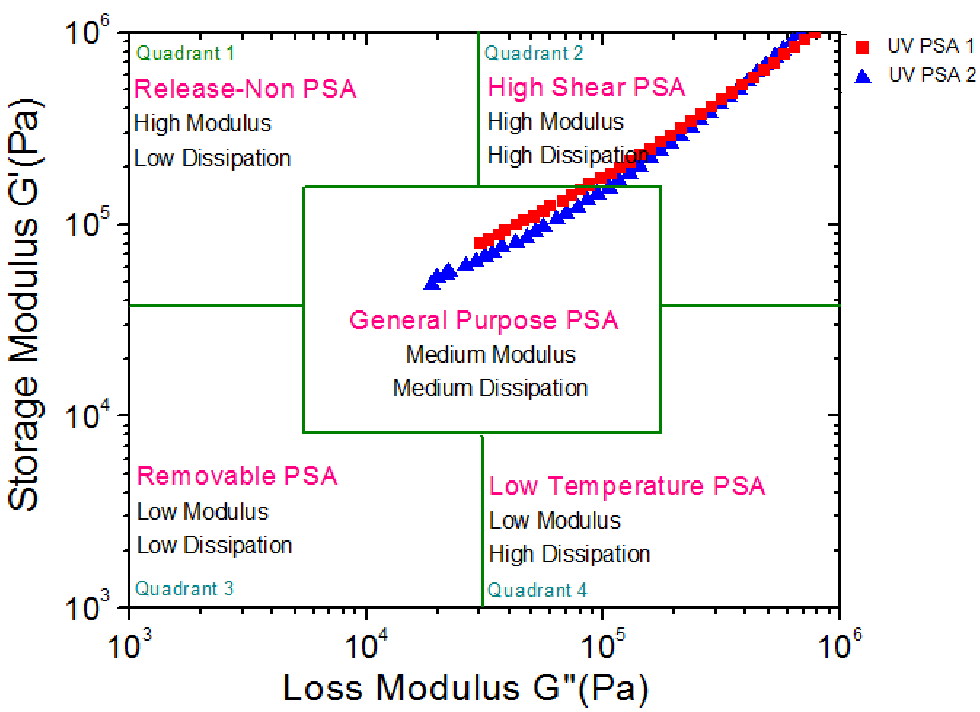

Figure 3 (c) The potential applications of UV PSA 1 and UV PSA 2 based on their viscoelastic properties.

Based on the special designed functional oligomer and fine manipulation of rheology properties of the formulations, the new UV curable syrup PSA products were developed. They could achieve high peel and high tack adhesion properties on both hydrophilic (such as stainless steel) and hydrophobic substrates (such as polypropylene) at room temperature.

PRO12423 shows excellent adhesion on stainless steel, polypropylene and untreated film PET. It also shows reasonable shear resistance. This product is suitable for a variety of different industry applications, such as permanent tape or transfer films.

Table 1. UV-PSA Performance of UV PSA PRO13243.

Product Code	**PRO13243**
Viscosity at 25°C (cPs)	15,500
Film Properties	
Thickness (mil)	5
Curing Energy (J/cm^2)	0.97
180 Peel on Stainless Steel (lb/in) , 3 days dwell	9.6
180 Peel on Polypropylene (lb/in), 3 days dwell	6.7
180 Peel on PET (lb/in), 3 days dwell	7.5
Probe Tack (lb)	2.2
Shear (hr), 2kg weight	4.5
Shear (hr), 1kg weight	23.5

PRO13253 shows higher shear resistance, improving the shear resistance 4 times longer at the expense of peel strength. Overall, it presents balanced peel and tack adhesion and shear resistance. It is suitable for a variety of industry and commercial tape applications. Preliminary studies also indicate these two products have good heat resistance. The PSA performance can be maintained after exposure to 150°C for 3 hours.

Table 2. UV-PSA Performance of PRO13253

Product Code	PRO13253
Viscosity at 25°C, cPs	6533
Film Properties	
Thickness (mil)	5
Curing Energy (J/cm^2)	0.97
180 Peel on Stainless Steel (lb/in), 3 days dwell	5.8
180 Peel on Polypropylene (lb/in), 3 days dwell	4.1
Probe Tack (lb)	1.6
Shear (hr), 2kg weight	21.2
Shear (hr), 1kg weight	108

Conclusion

Solventborne PSA continue facing the challenge of low VOC regulations. The specialty solventborne systems are difficult to be replaced by hotmelt or waterborne PSA systems due to their high performance requirements. In this paper, radiation curable technology demonstrates its unique advantage in offering such high performance. By special design of functional oligomers and tailoring the formulations, UV curable syrup PSAs can offer the high peel and tack adhesion to both high and low surface energy substrates and high cohesion at room temperature. The adhesives can be easily coated at room temperature or slightly warm temperature as needed to cure up to 5 mil thickness.

References

1. Viscoelastic Properties of Pressure Sensitive Adhesives, The Journal of Adhesion, 60:1-4, 233-248.
2. C. A. Dahlquist. Proc. Nottingham Conference on Adhesion. Part III, Chapter 5, p. 134.

Acknowledgment

The author would like to thank Jinping Wu’s dedicated application work, and Zeena Cherian’s rheology work.