UV Curable Solution Acrylic PSA with Optical Clarity

John Ouyang & Ingrid Brase
Henkel Adhesive Technologies
10 Finderne Ave
Bridgewater, NJ 08807
Tel: 908-685-5450
john.ouyang@us.henkel.com

A new Ultra Violet (UV) curable solution acrylic polymer based technology has been under development for manufacturing optically clear pressure sensitive adhesives. Monomers, functional groups, and formulating components can be selected to modify and tailor product properties for specific optically clear end uses. Refractive index, outgassing, heat resistance, and humidity resistance among other properties can be balanced along with traditional pressure sensitive adhesive properties such as peel, tack, and shear.

The UV curable solution acrylic pressure sensitive adhesive combines traditional solution acrylic and UV technologies. The marriage of these two technologies permits the products to be coated using existing solvent coaters (with an investment in UV lights) which can yield a level of coating quality difficult to achieve for thin films using traditional hot melt coating techniques. The UV curable solution acrylic PSA also provides a cleaner and more effective way of crosslinking through covalent bonds rather than the traditional ionic or covalent means. This enables PSA products to be developed and possibly coated at high solids levels while achieving performance of comparable high molecular weight (and low solids) adhesives.

Introduction

Acrylic pressure sensitive adhesives (PSAs) have been used in many applications where optical clarity may be required. The more traditional applications include transparent tapes, graphics, films and labels such as window & safety films, window advertising, and overlaminating. More recently, acrylic PSAs with optical clarity have been used in high tech applications such as fiber optics and electronic displays. The new applications have high performance requirements, e.g., more balanced adhesion, superior optical properties, and heat / humidity resistance. The current technologies use two-part adhesive systems consisting of extremely high Mw solution acrylic polymers that require further chemical crosslinking. The two-part adhesive systems with polymers of high Mw have to be used at a very low solid level. The chemical crosslinking is usually a slow and long process. The display industry has been looking for a one-part adhesive system that can provide all the performance benefits of the two-part systems but without the disadvantages. We have been developing an optically clear UV curable solution acrylic PSA to meet the display industry needs. The UV curable solution acrylic PSA with optical clarity is a one-part adhesive. The UV curable PSA has advantages over a chemically crosslinkable adhesive, e.g., high solid formulation, fast curing process, and effective inventory management. UV cure technology is viewed by display industry as a future trend in the manufacturing of display devices.

The optically clear UV curable solution acrylic PSA is developed by leveraging our technical capabilities in solution acrylic polymerization, window film pressure sensitive adhesives and UV curing technology. The UV curable PSA can be used on a variety of transparent substrates, e.g., glass, to manufacture optically clear objects. One application we are targeting at is for the manufacture of TFT-LCD. The UV curable PSA models our window film PSA. Optical properties such as light transmission and refractive index have been optimized through careful selection of monomers in polymer design. The UV curable PSA has improved peel adhesion and shear strength on a number of transparent substrates by utilizing various functionalities. It has demonstrated high resistance to heat and humidity aging. As the UV curable PSA is formulated in solution, it can be used to make high quality coatings with optical properties superior to hot melt coatings. The UV curable PSA can be cured at a much faster rate compared to the current technologies in use, providing potential benefits to TFT-LCD manufacturer in cost control.

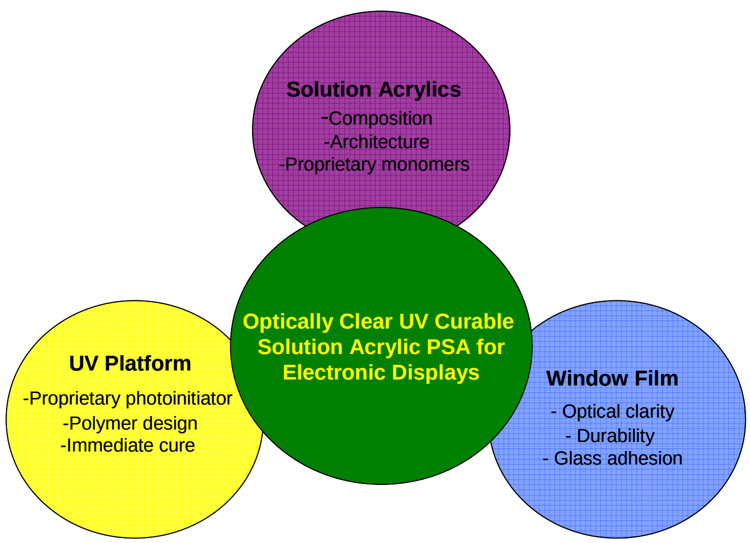

Figure 1. Leverage of Technical Capabilities

Design of UV Curable Solution Acrylic PSA with Optical Clarity

Acrylic copolymers have been used to produce PSAs for over 50 years. There is a wide range of acrylic and methacrylic monomers available for PSA development, providing chemists with great product design freedom. These acrylic and methacrylic monomers are characterized by their drastically different glass transition temperatures due to the difference in molecular polarities, which makes it possible to control the viscoelastic properties of an acrylic PSA for diverse performance.

Adhesion properties of the acrylic PSAs can be tailored by varying acrylic copolymer composition. Acrylic PSA products are based on a composition consisting of a soft, a hard, and a functional segment as shown in Figure 2. The soft segment is typically made of butyl acrylate, 2-ethyl hexyl acrylate, octyl acrylate or any other soft monomers. A hard segment is typically made of a smaller quantity of methyl acrylate, methyl methacrylate or any other hard monomers. Functional monomers like acrylic or methacrylic acids are frequently incorporated into the acrylic polymers for greater formulation latitude and ability of PSA modification.

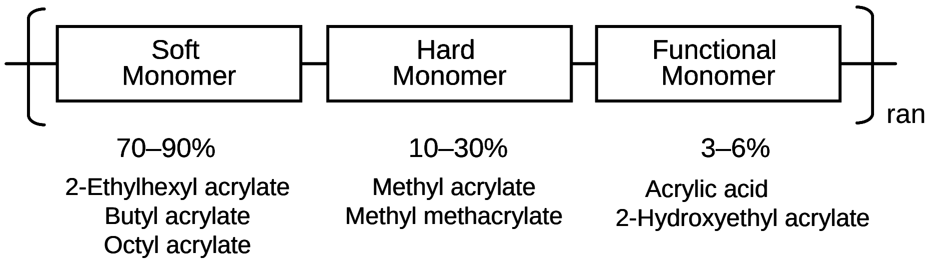

Figure 2. Typical Acrylic PSA Polymer Composition

Factors that Influence Optical Properties of PSA

There are three main factors that can influence optical clarity of a PSA product: (1) chemical structure of PSA polymers; (2) morphology of the polymers; (3) coating quality.

The chemical structure of a polymer at molecular level determines the optical properties depending on whether there is any light absorbing component in the polymer. Acrylic PSAs generally have good optical clarity due to the lack of strong electronic transitions upon excitation with UV-Vis light radiation. As shown in Figure 3, the possible electronic transitions upon excitation in the UV-Vis region are a weak $n \rightarrow \pi^*$ transition at 290 nm with ε = 15 (liter mol-1cm-1) and a moderate $\pi \rightarrow \pi^*$ transition at 180 nm ε = 10,000 (liter mol-1cm-1) in the C=O double bond. Both electronic excitation transitions are outside the visible region of 400 – 700 nm.

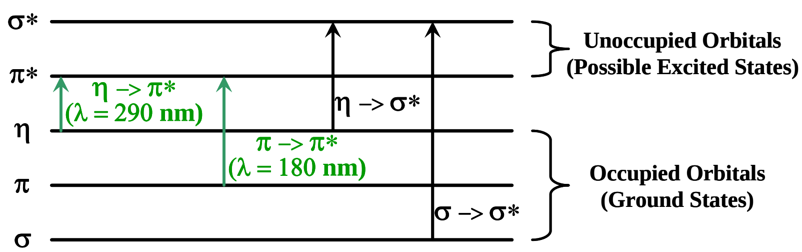

Figure 3. Electronic Excitation of C=O in Acrylate

Furthermore, refractive index affects the path of light propagation and the overall optical clarity. A close match of the refractive index between the coating and substrate ensures a better clarity. Acrylic PSAs typically have a refractive index >1.47 and can be easily optimized to match application substrate through the acrylic polymer composition adjustment.

Acrylic copolymers tend to be optically clear also because they are typically amorphous, not semi-crystalline, due to the various pendent groups. Any micro-domain formation due to phase separation can cause a decrease of optical clarity if the domain size is larger than the wavelength of visible light.

Optical clarity can only be achieved when the refractive index is constant through the coating in the viewing direction. A high quality coating free of various optical defects can avoid light loss caused by refraction, scatter, and diffusion. Our UV curable PSA is made in solution. The product form we have chosen makes it possible to make high quality coatings free of these defects. Figure 4 shows various light loss mechanisms when a light beam passes through an imperfect PSA coating.

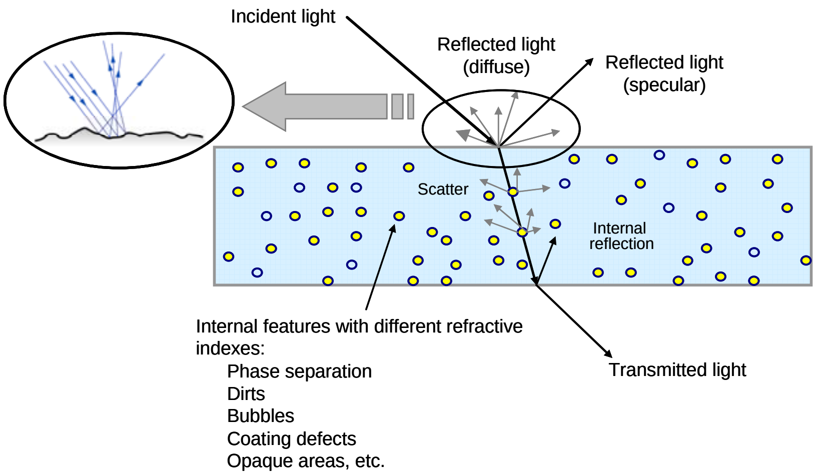

Figure 4. Coating Quality Impact on Optical Clarity of Coatings

UV Cure Technology

Crosslinking is an effective method of modifying mechanical and adhesion properties of PSAs. A PSA can be crosslinked either by chemical interactions or by UV radiation. Chemical crosslinking has been widely used in PSA product development for many years. Although chemical crosslinking is versatile and easy to use, the curing process is slow and often requires a two-part adhesive formulation. UV curable PSAs have become a technology of choice in the PSA industry in recent years. UV curing is easy to control and a fast process. Figure 5 shows a general UV crosslinking process with a polymer bound photoinitiator.

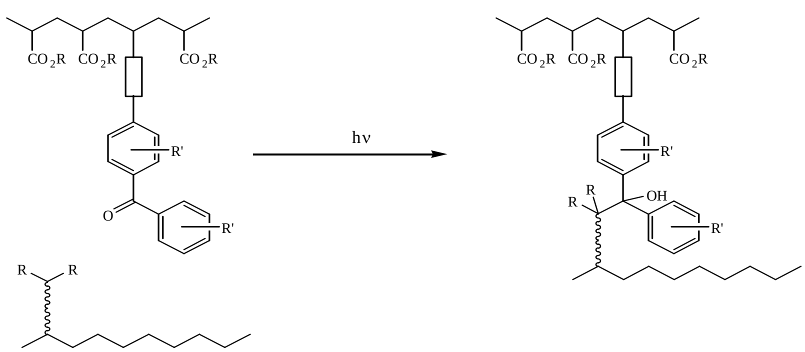

Figure 5. UV Curing Process

When designed properly, an UV curable solution acrylic PSA can be formulated at a much higher solid than a chemically crosslinked solution acrylic PSA with similar performance. It requires less drying time when the high solid UV curable solution acrylic PSA is coated, which can possibly reduce the overall run time in production. This, in turn, can potentially increase production capacity and throughput rates.

Characterization of UV Curable Solution Acrylic PSA with Optical Clarity
Following the design principles for the UV curable PSA with optical clarity, we have developed prototype polymers that can be further formulated for specific applications. The polymer composition models a solution acrylic window film PSA and uses acrylic monomers with high transmission in the visible region and high refractive index to ensure the optical clarity. The polymer further contains various functional groups that can facilitate specific interactions with different parts of the polymer and application substrate. Coupling agent is incorporated in the polymer to enhance the interaction with glass and impart humidity resistance. To achieve instantaneous UV curing and avoid any delayed or "dark" curing, a radical cure system has been chosen. A more efficient polymer-bound photoinitiator has been used in the UV curable PSA. Since such species are already a part of the polymer, and only one reaction is needed in order to create a crosslink between two polymer chains, the curing efficiency is high compared to at least two reactions with an unbound photoinitiator. A proprietary polymer-bound photoinitiator with a molecular structure similar to those shown in Figure 6 is reacted into acrylic polymer.

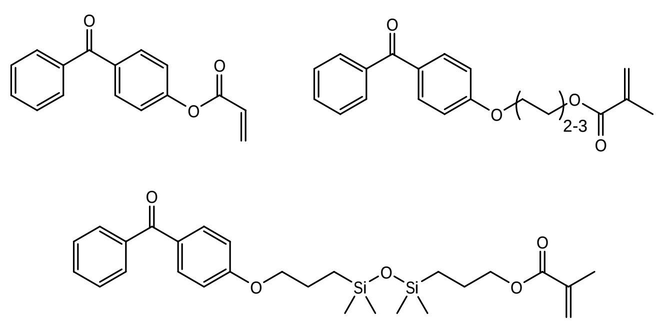

Figure 6. Functionalized Benzophenones

While the detailed composition is proprietary, the building blocks and functions of each building block and typical functional monomers are shown in Figure 7 to demonstrate the ideas and principles of product development.

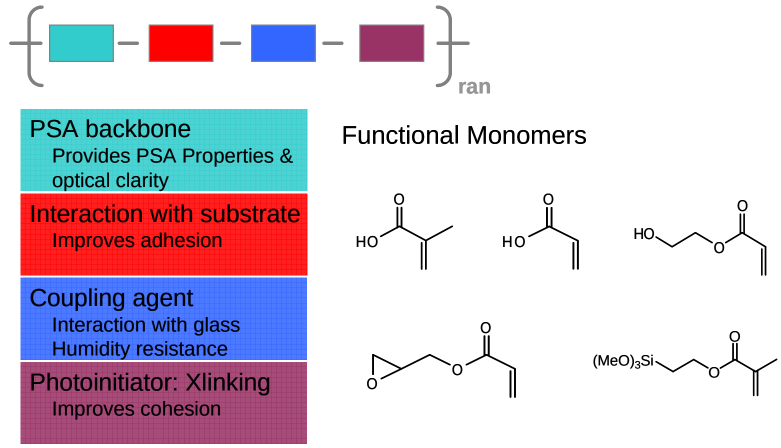

Figure 7. UV Curable Acrylic Polymer Design and Functional Groups

The UV curable acrylic PSA has been evaluated extensively for properties important to the manufacturing of TFT-LCD. It has been compared with various commercial technologies that are currently used in display industry. The commercial products are solution acrylic based and use polymers with Mw over 1 million. To further build the shear holding strength, the commercial products are usually hydroxyl functionalized and crosslinked with isocyanate. Table 1 compares the UV curable PSA with commercial products.

Table 1. Comparison between UV Curable and Current Technologies

	UV Curable Technology	Current Technology
Product Design	UV Solution acrylic	Solution acrylic
Optical Clarity	Excellent	Excellent
Product Form	1 Part system	2 Part system
Curing Mechanism	UV Radiation	Chemical XL
Curing Rate	Fast (Instant)	Slow (Up to 7 days)
Solid Level	Medium - High (40 - 60%)	Low (20%)

The UV curable solution acrylic PSA has good coatability. We are able to make coatings with various coat weights from 0.2 to 2 mils. Clear and uniform coatings have been obtained. After coated on a clear release liner and dried in an oven to remove the solvent, the adhesive is cured using UVC. A 1-mil coating can be fully cured with 40 – 50 mJ/cm^2 of UVC. We have used Confocal Raman microscopy to assess the completeness of the coating curing. The C=C bond from crosslinker molecules that are formulated into the UV curable PSA disappears completely upon the UV radiation, as shown in the Confocal Raman microscopy spectra in Figure 8. Confocal Raman microscopy was also used to map the depth profile of UV curing through a 1 mil coating.

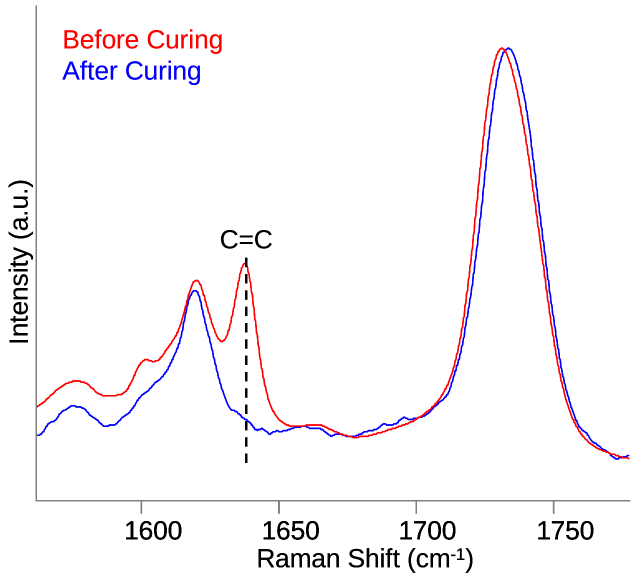

Figure 8. Confocal Raman Microscopy of UV PSA Coatings (1 mil)

A uniform curing of the coating throughout the entire depth was achieved with UV exposure at 43 mJ/cm^2. The Raman spectra at various depths from top to bottom layer are very similar as shown in Figure 9.

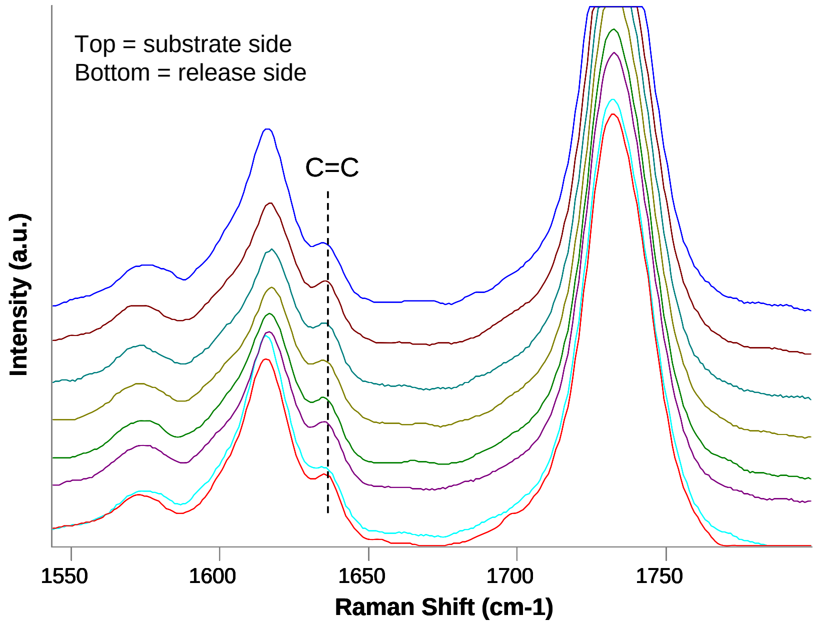

Figure 9. Confocal Raman Microscopy
Map through UV curable acrylic PSA (1 mil) Cured at 43 mJ/cm^2

UV curing effect on the UV curable PSA has been evaluated with dynamic mechanical analysis (DMA). Figure 10 is a plot of modulus and tan(δ) as a function of temperature for the PSA before and after UV curing with 40 mJ/cm^2 of UVC. The PSA before and after UV curing displays an identical peak in tan(δ) curves, which means that UV curing does not change the glass transition temperature of the PSA. The most striking effect of the UV curing is the improvement of the cohesive strength of UV cured PSA at high temperatures. The PSA before UV curing shows the modulus as a function of temperature for a typical acrylic PSA. As the temperature increases, the PSA transitions from glassy to rubbery state when the temperature crosses the glass transition temperature. The PSA reaches a rubber-like, slowly varying plateau region. The decrease of modulus accelerates when the temperature further increases. Eventually the PSA can act as a purely viscous liquid. The length of the rubbery plateau increases with molecular weight. When the PSA is crosslinked, the PSA can stay at rubbery state even at higher temperatures. Figure 10 clearly shows the difference in the PSA modulus before and after UV curing. The modulus of the PSA before UV curing drops more quickly when the temperature increases beyond 80°C. After UV curing the modulus remains a nearly constant plateau of the rubbery state.

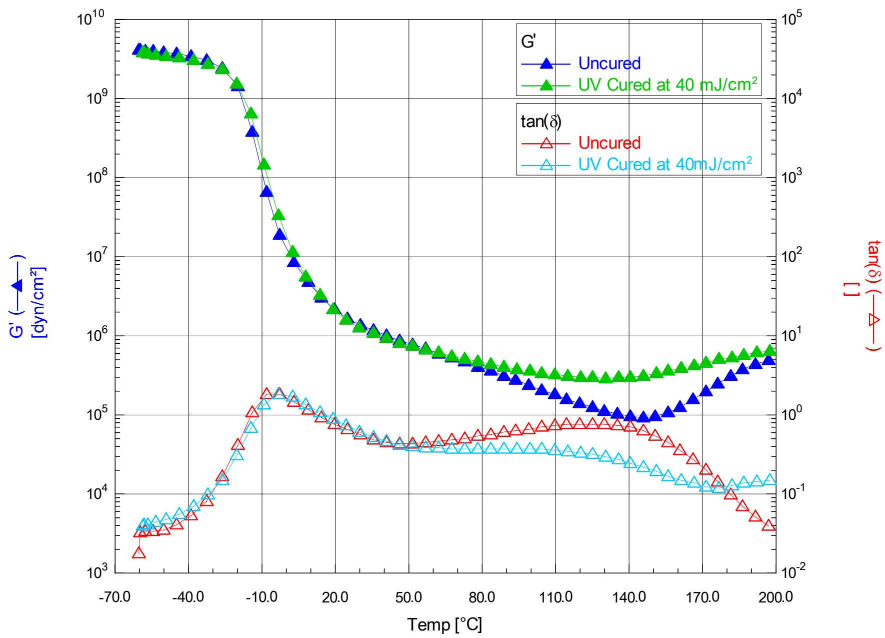

Figure 10. Temperature Dependence of G' and tan(δ) for PSA

The optically clear UV curable solution acrylic PSA has been evaluated for adhesion performance. Peel force values of the PSA after UV curing have been measured on a variety of application substrates. The UV cured acrylic PSA shows excellent adhesion on all tested substrates including glass and polycarbonate as shown in Figure 11. Glass and polycarbonate are optically clear substrates used widely in electronic display devices. The optically clear UV curable acrylic PSA has been compared with two commercial solution acrylic PSA products that are chemically crosslinked. The adhesion performance of the UV curable acrylic PSA is either equal to or better than that of the commercial products.

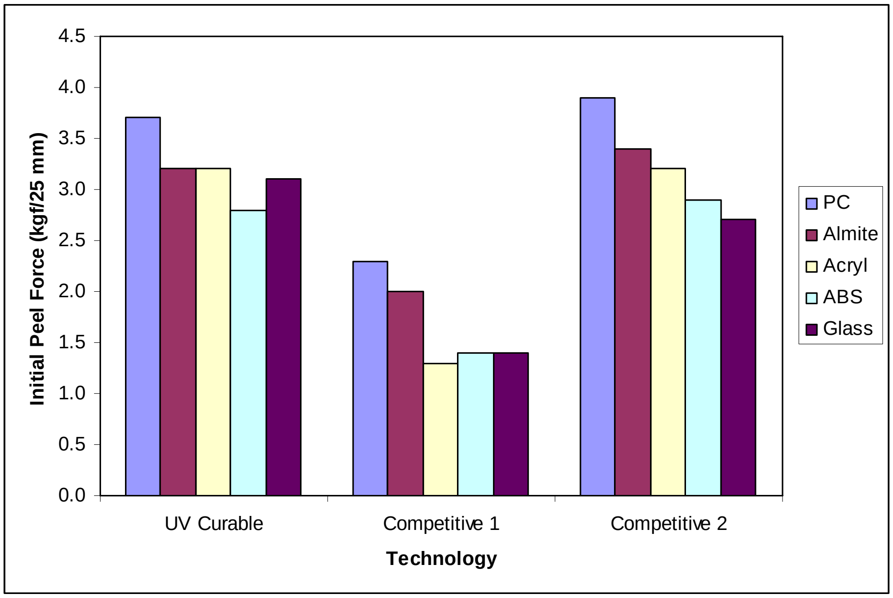

Figure 11. Peel Adhesion on Various Substrates

For a PSA used in many electronic display applications, the PSA is often required to perform under various environmental conditions. Figure 12 compares the UV curable PSA with the two commercial chemically crosslinked products for their resistance to heat and humidity aging. In peel tests after aging at 80^{o}C / 85% RH, the UV curable acrylic PSA outperforms the two commercial solution acrylic PSAs.

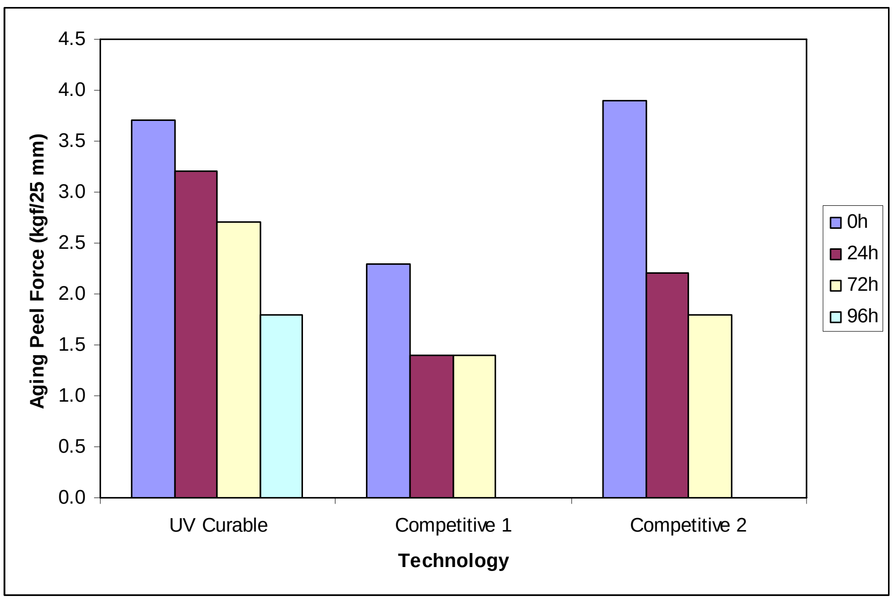

Figure 12. Resistance to Aging at 80^{o}C & 85% RH

The optically clear UV curable solution acrylic PSA can be formulated in a wide range of viscosities to meet specific customer coating requirements. There is a variety of polymer composition parameters that can be used to tailor the performance of the optically clear UV curable PSA. Many solution acrylic PSA formulation tools can also be used to finetune the optically clear UV curable solution acrylic PSA for further improvement of performance.

Summary
A new UV curable solution acrylic pressure sensitive adhesive with optical clarity is being developed by leveraging Henkel's capabilities in solution acrylic polymerization, window film pressure sensitive adhesives and patented UV curing technology. The free radical UV curable solution PSA can offer several benefits compared to chemically crosslinked adhesives: instant cure, one-part system, and efficient coating with high solids. The fast curing reaction allows for a high-speed coating process and eliminates the long holding time needed for build-up of curing, resulting in improving cost efficiency. The UV curable PSA has excellent adhesion on a variety of application substrates and outperforms chemically crosslinkable PSA in heat and humidity aging tests. The UV curable solution acrylic PSA is ideally suited for applications with requirement of optical clarity and represents the future technology trend in adhesives for the display industry.