Abstract
The development of UV curable hot melt pressure sensitive adhesives (PSAs) has progressed significantly over the last few years. Some UV products have similar performance attributes as solution PSA products, but without the need for expensive drying ovens and incinerators. Therefore, the applied cost of the UV hot melt PSA can be significantly lower than solution products. This is especially true for PSA applications requiring thicker films, where solution drying lines must run slowly to obtain quality coatings. This paper introduces a new technology that permits the generation of UV curable hot melt PSAs with solution-like performance even at high film thickness. The products can be applied on conventional hot melt coaters at a temperature range of 100-120°C at reasonably high line speeds. A broad range of products are possible with this technology, including applications for high or low temperatures, high cohesive strength, and low surface energy (LSE) adhesion. Good cure-thru of films as thick as 10 mil (250 microns) has been validated. These UV curable hot melt PSAs can be considered to be a viable alternative to solution PSAs for industrial tape applications.

Introduction
UV curable hot melt PSA has been an area of interest for the past several decades. Compared with solvent based PSAs (typically around 40-55% solids), 100% solids hot melt PSAs offer a more efficient avenue to create thicker adhesive film. Traditional hot melt adhesives are mainly rubber-based adhesives, which might have some limitations in performance and have poor weatherability. Acrylic UV curable hot melt PSAs, with the right design, would provide a solution combining the advantageous processing, balanced performance and good weatherability.

Multiple approaches have been reported to generate UV curable hotmelt PSA. Below are some examples:
a) Bound type II photoinitiator in acrylic polymer backbone by co-polymerization of acrylated benzophenone and the like with acrylic monomers1,2;
b) Further formulation of bound photoinitiator adhesives with multi-functional crosslinkers and other additives to enhance performance3;
c) Adhesives based on polyurethane with acrylate functional groups4;
d) Adhesives based on acrylate functionalized acrylic polymers5;
e) Rubber based PSAs with bound or added photoinitiators6;
f) Cationic cure UV PSA based on acrylic polymer with epoxy functionality7.
For each of the above approaches, curing mechanism and performance balance may vary. This paper is focused on the technical approach of acrylate functionalized acrylic polymers and formulation to achieve balanced performance. The rheology and processing of UV curable hot melt PSAs and curing of the adhesive are discussed as well.

Experiments

Polymerization and formulation
A hydroxy-functionalized acrylic polymer was made and reacted with a derivatizing agent. The derivatizing agent was prepared from diisocyanate and a hydroxy-functional acrylate monomer. The process generated an acrylate-functional acrylic polymer. The polymer was further formulated with appropriate photoinitiator and other additives, such as tackifier, crosslinking agents, stabilizer, inhibitors, plasticizers and the like.

The polymerization and formulation process can be carried out in a solvent, which would be removed to produce 100% solids hot melt adhesives.

Melt Viscosity Measurement
Viscosity profile of UV curable PSA is generated by measuring melt viscosity at various temperatures (from 90°C to 115°C) using Brookfield RVDV-II+PRO with Thermosel Accessory. A disposable spindle and cylinder are used, to avoid contamination. For each temperature, viscosity data was obtained after equilibrium. The viscosity profile provides a reference for adhesive processing temperature.

Film Preparation
Films can be prepared from solution or hot melt adhesives. Films at 2 mil to 5 mil were drawn down from solution followed by a 15~30 minutes air dry and a 10~30 minutes oven drying at 100°C. Higher coat weight (>5 mil) is preferably coated from hotmelt adhesives.

The films were coated on release liner and then cured in air by UV radiation. Fusion DRS-10/12QNH lab unit is operated in the power class of 600 watts/in and equipped with 10 in H-bulb. The unit provided UVC (wavelength of 200-280nm) dosage up to 200mJ/cm². UV Power Puck II and MicroCure MC-10 from EIT were used for UV radiation measurement. Adhesive films were cured at different UVC dosages to determine the optimal curing condition.

The cured films were laminated to 2-mil Mylar film for performance testing.

Adhesive Performance Testing
All performance testing was carried out in a controlled environment with constant temperature (23°C) and humidity (50% RH) unless otherwise noted. Table 1 listed the test methods.

<table>
<thead>
<tr>
<th>Performance Aspects</th>
<th>Test Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peel Adhesion</td>
<td>PSTC-101&lt;sup&gt;8&lt;/sup&gt;</td>
</tr>
<tr>
<td>Loop Tack</td>
<td>PSTC-16&lt;sup&gt;8&lt;/sup&gt;</td>
</tr>
<tr>
<td>Shear at Room Temperature</td>
<td>PSTC-107&lt;sup&gt;8&lt;/sup&gt;</td>
</tr>
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Results and discussion

Design of acrylate functional acrylic polymers
The design of acrylic polymers is one of the key determining factors for processability and performance. Acrylic base polymers were prepared via free radical polymerization from the following monomer groups or their combinations: a) monomers with low glass transition temperature (Tg), such as 2-ethylhexyl acrylate, iso-octyl acrylate, n-butyl acrylate and the like; b) monomers that modify Tg, such as methyl acrylate, ethyl acrylate, methyl methacrylate, vinyl acetate and the like; c) monomers with special functional groups, such as acrylic acid, glycidyl methacrylate, N-vinyl pyrrolidone, and acrylamide; d) hydroxy-functional acrylic monomers, such as 2-hydroxyethyl acrylate/methacrylate, 2-hydroxypropyl acrylate/methacrylate, 4-hydroxy butyl acrylate and the like. Theoretical Tg can be calculated from the combination of monomers using the Fox equation. Tg of the acrylic base polymer should be well below the application temperature, to ensure good PSA properties in application. During the polymerization step, the molecular weight (Mw) of the base polymer was designed and controlled to be about 100,000-150,000. A too low molecular weight may sacrifice performance and a too high molecular weight may pose challenges for hot melt processing.

The derivatizing agent is typically prepared from a diisocyanate and a hydroxy-functional acrylate monomer. By optimizing the catalyst package and reaction condition, the hydroxyl-functional acrylate monomer will react preferably with one isocyanate group and leave the other isocyanate intact for later derivatization reaction with hydroxyl group on the acrylic base polymer backbone.

In the derivatization step, the acrylic base polymer is reacted with a pre-determined amount of derivatizing agent. The ratio between acrylic base polymer and derivatizing agent determined the crosslinking density of the UV curable PSA. An example of the resulting acrylate functional acrylic polymer is shown in Figure 1.

![Figure 1. Functionalized acrylic polymer for UV curable PSA formulation](image)

Formulation of UV curable PSA
Besides functionalized acrylic polymers, UV curable PSA formulations typically comprise photoinitiators and additional additives, including but not limited to stabilizers, tackifiers, crosslinking agents, reactive diluents, plasticizers, fillers and plasticizers.

Based on the initiation mechanism, photoinitiators can be divided into Norrish Type I and Type II initiators. Type I initiators undergo a unimolecular cleavage into two radical species upon UV radiation and may initiate polymerization of active acrylic functionality. Examples of Type I photoinitiators include benzoin derivatives, benzil ketals, α-hydroxyalkylphenones, α-amino acetophenones, acylphosphine oxides and the like. Type II initiators form radicals through hydrogen abstraction or electron transfer from a co-initiator. Examples of Type II photoinitiators are mainly based on aromatic ketones, such as benzophenone, thioxanthones and camphorquinones. Each photoinitiator has its own absorbance characteristics. Combinations of photoinitiators may be used to achieve good balance of surface cure and through cure, which is critical for coating thicker films.

For low surface energy adhesion applications, a tackifier is typically used in acrylate polymers. Rosin esters, preferably hydrogenated rosin esters, have been proven to be compatible and effective. Hydrocarbon C₅ and C₉ tackifiers may also be considered. The loading of the tackifiers may range from about 10-30% of the total formulation.

**Hot melt processing and curing**

To ensure good coating quality, viscosity profile and rheology of the adhesives are taken into consideration while setting up coating parameters. Figure 2 shows the viscosity of two UV PSAs as a function of temperature. As temperature increases, the melt viscosity decreases. Melt viscosity of the adhesive is closely related to molecular weight, glass transition temperature (Tg) of the polymer, interaction between molecules, and additives in the formulation. The processing temperature may range from 100°C to 120°C depending on the equipment and coating method involved. Although knife over roll, roll coater and other coating method can be used in UV curable PSAs, slot die coating is highly recommended to achieve precise control and good coating quality.

![Figure 2. Melt viscosity profile of various UV curable PSAs](image-url)
Understanding the adhesive rheology is equally important, since the adhesive is under shear condition for various coating methods. Adhesive response to shear can be characterized by using capillary rheology. The rheology data can be analyzed and imported in simulation models, which can be further used to predict coating behavior and improve design of coating equipment.

Figure 3. Diagram of coating and curing UV curable PSA

Figure 3 showed the diagram representing a typical coating and curing process of UV PSAs. The process involves melting and transfer of the adhesive using a drum melter (a reservoir may be applicable if the adhesive throughput requirement is beyond the maximum delivery capacity of a drum melter); coating on a substrate or release liner; and curing under UV radiation. UV hotmelt processing tends to have a smaller footprint than solvent PSA processing by eliminating the drying oven. For higher deposition coating, UV hot melt PSA generally allows coating at faster line speed than solvent PSA coating assuming enough UV dosage is provided.

Figure 4. UV curable PSA cure window of 2mil films
When curing UV PSAs, UV energy density (or dose) determines the performance of the cured adhesive films. Adhesive suppliers typically provide a curing guide with PSA performance as a function of UV dose for various coat weights. Figure 4 is an example of UV PSA cure window at 2 mil (50 micron) coat weight. As UVC dose increases, 180° peel value decreased and leveled off at around 40 mJ/cm² while shear performance continued to improve and reached a plateau around 60 mJ/cm². Based on the above data, UVC dose of ≥ 60 mJ/cm² is recommended to achieve consistent performance. UV energy density and distribution is determined by the type of lamp, lamp irradiance, and exposure time (or line speed). A radiometer can be used to measure the energy density at various line speeds to build an energy map. However, it’s more accurate and easier to measure the energy at a lower speed and used the information to calculate for higher line speeds using the equation below:

\[ E_y = E_x \times \frac{V_x}{V_y} \]

Where E stands for the UV energy at certain line speed of V.

Since the adhesive performance is highly dependent on UV dose, monitoring UV dose and QC testing to ensure optimal curing are critical. For continuous monitoring, online monitoring system can be used, but generally is associated with higher overall cost. Performance data indicated that peel adhesion is less sensitive to UV dose than cohesive strength. QC methods that related to cohesive strength could be considered to determine the degree of curing, such as static shear at ambient or elevated temperature, dynamic shear, Williams Plasticity, force retention test and so on. Force retention value can be calculated from stress relaxation over a short period of time (such as 4 minutes) using a Texture Analyzer. This technique gives rapid and reproducible measurement of cohesive strength of the adhesive film. Figure 5 showed the force retention⁹ value of 2 mil films of UV PSA cured at various UVC dose. Force retention started to level around 50 mJ/cm². It indicated that cohesive strength of 2 mil films reached a plateau when UVC dose is ≥ 50 mJ/cm².

Figure 5. Force retention of UV PSA film cured at various UVC dosages

UV PSA based on this technology can achieve good cure-thru even at higher deposition (as thick as 10 mil or 250 micron). Cure window study at different coat weights provides recommendations on UVC dose to achieve optimal curing. Table 2 listed typical PSA performance of 2 mil and 5 mil films of UV
PSA 1 and UV PSA 2. UV PSA 1 is designed for industrial tape applications and UV PSA 2 can be used in general tape applications.

Table 2 Typical performance of UV PSAs

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>UV PSA 1</th>
<th>UV PSA 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desirable applications</td>
<td>LSE industrial tape</td>
<td>General tape</td>
</tr>
<tr>
<td>Coat weight of transfer film</td>
<td>2 mil</td>
<td>5 mil</td>
</tr>
<tr>
<td>Loop Tack (lb/in²)</td>
<td>5.4</td>
<td>7.6</td>
</tr>
<tr>
<td>180° Peel—SS 24h dwell (lb/in)</td>
<td>4.3</td>
<td>4.8</td>
</tr>
<tr>
<td>180° Peel—PP 24h dwell (lb/in)</td>
<td>4.2</td>
<td>6.2</td>
</tr>
<tr>
<td>180° Peel—HDPE 24h dwell (lb/in)</td>
<td>2.1</td>
<td>2.5</td>
</tr>
<tr>
<td>1”x1”x1Kg Ambient Shear (hrs)</td>
<td>700+</td>
<td>300+</td>
</tr>
</tbody>
</table>

- Film cured at recommended UVC dose
- All samples were transfer to 2mil Mylar face stock

Performance Space

Figure 6. Performance space of cohesion and adhesion

The properties that are essential for pressure sensitive adhesives comprise tack, peel adhesion and shear. Tack and peel are typically used to characterize adhesion, whereas cohesion can be described by shear resistance. The balance of adhesion and cohesion is characteristic to pressure sensitive adhesives. The following design factors will determine the final properties of UV PSAs: a) design of the base polymer, which includes the selection of monomers, molecular weight of the base polymer, usage of special functional monomers; b) polymer network and crosslinking density; c) UV-induced curing mechanism and efficiency; d) formulations with additives, such as tackifier, fillers, and crosslinkers. Figure 6 shows the concept of performance space. There are three product families that each have a different balance of adhesion and cohesion.

Conclusions
A new technology of making UV curable PSAs is described in this paper. An acrylic polymer was prepared via free radical polymerization, followed by a derivatization step to introduce acrylate functionality to the polymer backbone and then formulation with photoinitiators and other additives. The resulting hot melt adhesive can be applied on a conventional hot melt coater at temperatures ranging from 100-120°C. Curing of the adhesive films (up to 10 mil thick) can be achieved by UV radiation. By controlling the design of base polymer, degree of derivatization and formulation, products with a different balance of adhesion and cohesion can be developed to cover the performance space. For example, UV PSA 1 showed in the paper may be a good candidate for industrial tape applications where LSE adhesion is required.

References
10. Patrick Gloeckner (2009), Radition Curing Coatings and Printing Inks, Vincentz Network GmbH & Co KG