

# UV-CURABLE HOT MELT PSAs BASED ON STYRENIC BLOCK COPOLYMERS

Cynthia Cain, Senior Development Chemist, Henkel Corporation, Bridgewater, NJ

## Introduction

Traditional hot melt pressure sensitive adhesives (PSAs) provide many advantages over solution and waterborne technologies. These include high peel and tack, particularly on low surface energy substrates, and environmental advantages due to lack of VOCs or the need for drying of the solvent or water. One of their shortcomings, however, is performance at elevated temperatures. One method to combat this is through crosslinking with ultraviolet (UV) radiation. Some challenges in designing such an adhesive include selection of the appropriate photoinitiator, photoinitiator level and UV dose. The resulting adhesive can be designed to have a good balance of peel, tack, and shear, as well as good heat resistance, chemical resistance and UV stability.

## Background on Hot Melt PSAs

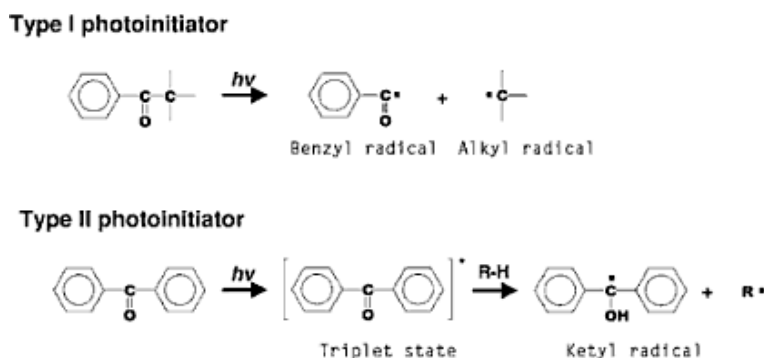
Hot melt pressure sensitive adhesives are traditionally based on styrenic block copolymers, such as styrene-isoprene-styrene (SIS) or styrene-butadiene-styrene (SBS). These polymers have a soft, elastomeric midblock and hard, glassy endblocks. Their unique design allows them to have a microphase separated morphology. As they cool, the endblocks aggregate to form domains or physical crosslinks surrounded by the rubbery midblock phase.<sup>1</sup> This is shown schematically in Figure 1.

**Figure 1.** Microphase separation of styrenic block copolymers.<sup>2</sup>

Hot melt PSAs obtain their strength and heat resistance through these thermally reversible physical crosslinks. Meanwhile, acrylic PSAs utilize high molecular weight and/or chemical crosslinking for cohesive strength. UV-curing technology offers the opportunity to chemically crosslink 100% solid rubber-based hot melt PSAs, while maintaining the benefits of hot melt processing.

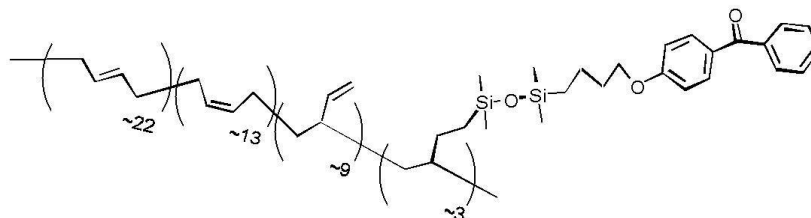
## Photoinitiator Selection

There are two categories of photoinitiators used to initiate radical crosslinking: Type I (photocleavage) and Type II (hydrogen abstraction). Figure 2 shows the process of radical formation for each.



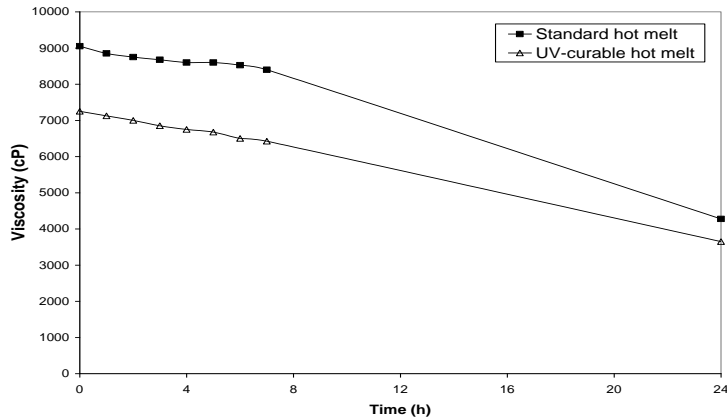
**Figure 2.** Two categories of free radical photoinitiators.<sup>3</sup>

Increasing concern over the presence of extractable small molecules in UV-cured materials has led to the development of polymerizable and polymeric photoinitiators. Polymerizable photoinitiators, which can be polymerized into the polymer backbone, are not an option for hot melt formulators, who have little control over styrenic block copolymer (SBC) design. Polymeric Type I photoinitiators are still a concern due to by-products generated during photocleavage. Utilization of a novel polymeric Type II photoinitiator allows for the possibility of zero extractables and can be synthesized in such a way as to be compatible with styrenic block copolymers and have excellent thermal stability. Figure 3 shows the structure of one such photoinitiator.



**Figure 3.** Polybutadiene-grafted benzophenone polymeric photoinitiator.<sup>4</sup>

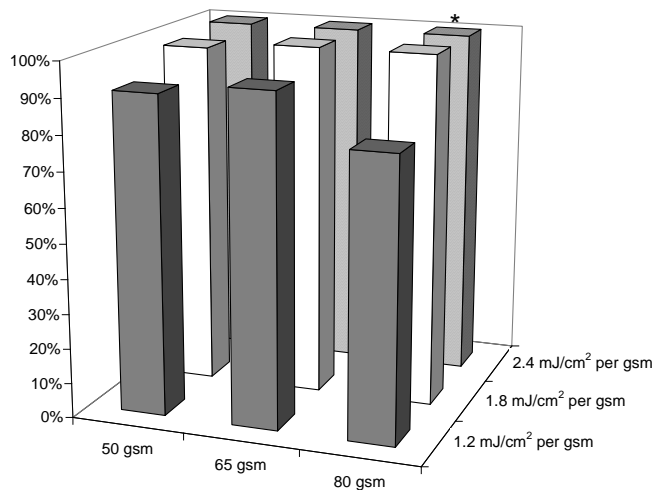
Thermal stability is an important requirement for hot melt adhesives. By measuring initial viscosity and then aging the adhesive in the viscometer at 350°F (177°C), we can compare the stability of formulations, with and without photoinitiator. Figure 4 shows a 7% viscosity drop after eight hours for the standard hot melt compared to 11% for the UV-curable formulation, a negligible difference. Both provide acceptable thermal stability and, most importantly, the addition of photoinitiator does not cause the adhesive to gel.



**Figure 4.** Viscosity response at 350°F vs. time.

### Formulation and Curing

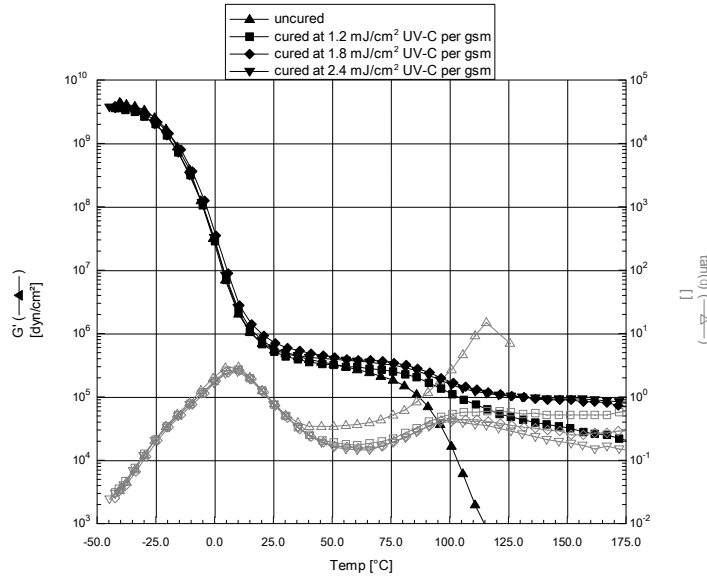
Selection of the proper UV dose is critical to overall adhesive performance. Figure 5 compares gel fraction results at three different coating weights and three different levels of UV exposure. This test involved soaking a free film of adhesive in toluene and then filtering, drying and weighing the adhesive that did not dissolve. We assume that only the polymer and photoinitiator will crosslink. For each coat weight there is a significant decrease in gel fraction when the film is exposed to 1.2 mJ/cm<sup>2</sup> per gsm (e.g. 60 mJ/cm<sup>2</sup> per 50 gsm), suggesting incomplete cure. This is more pronounced at 80 gsm. With higher UV exposure, gel fraction is approximately 100% for all coat weights, indicating that all of the polymer in the formulation has crosslinked. This suggests that 1.8 mJ/cm<sup>2</sup> per gsm is a sufficient UV dose across all three film thicknesses.



**Figure 5.** Gel fraction results at various coating weights and UV doses. (\*anticipated value)

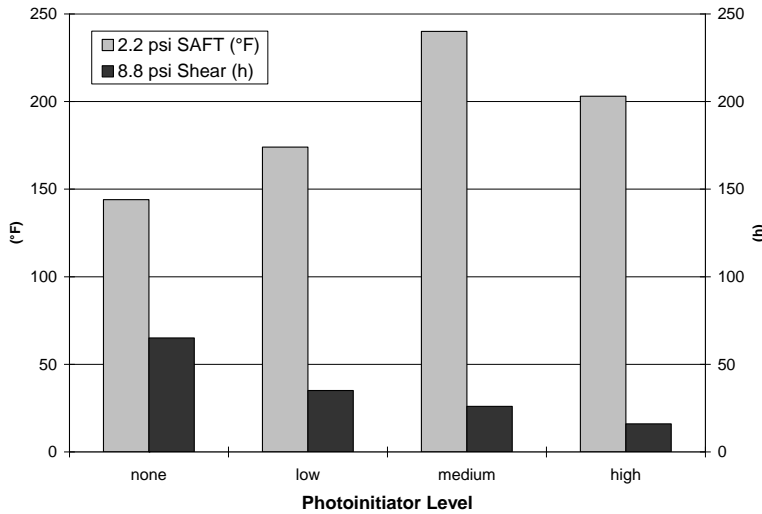
Like gel fraction testing, rheology is another tool that can be used to measure the bulk properties of a UV-curable hot melt. Figure 6 was made using a controlled strain rheometer with 8 mm parallel plate geometry, at a frequency of 10 rad/s. As the adhesive cures, there is a significant change in

the storage modulus ( $G'$ ) at elevated temperature, indicative of crosslinking. For this example, 1.2  $\text{mJ}/\text{cm}^2$  of UV-C per  $\text{gsm}$  does not fully cure the adhesive. The films that were exposed to 1.8 and 2.4  $\text{mJ}/\text{cm}^2$  of UV-C per  $\text{gsm}$  show a similar level of cure, but can be differentiated somewhat by their  $\tan \delta$  values. This corresponds nicely to the gel fraction results from Figure 5.



**Figure 6.** Rheological curve of UV-curable adhesive, before and after cure.

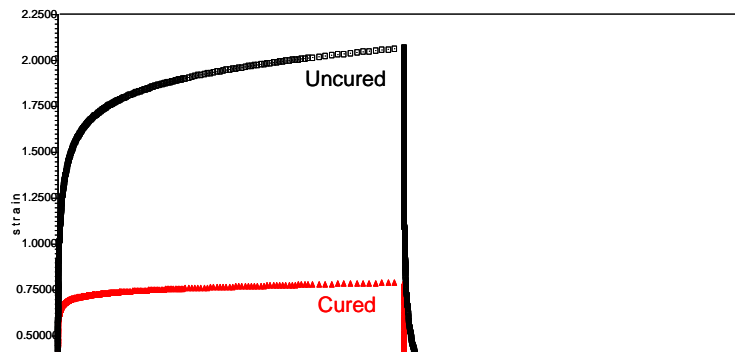
Choosing the correct photoinitiator (PI) level is also very important to the final PSA characteristics. Figure 7 shows the results of shear adhesion failure temperature (SAFT) testing, a measure of heat resistance, and shear holding power, a measure of cohesive strength, for several PI levels. The substrate is stainless steel.



**Figure 7.** PSA properties across photoinitiator levels, 50  $\text{gsm}$ , transferred to 2 mil PET, 90  $\text{mJ}/\text{cm}^2$  UV-C.<sup>5</sup>

As predicted, heat resistance is higher for all of the UV-cured adhesives, with improvements in SAFT of up to 65%. The low PI formulation appears to be insufficiently cured, which can be confirmed by its lower gel fraction and higher peel values. Shear holding power (8.8 psi load), on the other hand, is superior for the uncured hot melt. In theory, one would predict higher cohesion with the covalently crosslinked adhesive, however, the resulting cured adhesive may be too stiff and prematurely fail under high shear loads. With a less extreme load of 4.4 psi, the UV hot melt adhesive can hold for more than 1 week.

To further explore this decrease in shear at higher photoinitiator levels, creep recovery testing was done using a controlled stress rheometer with 8 mm parallel plate geometry. Figure 8 shows the creep of the cured and uncured adhesives during the initial 30 minutes of the test under constant stress and recovery during the final 30 minutes. Clearly the uncured adhesive creeps more than the cured adhesive, proving that the cured PSA does not lack cohesive strength. Its decreased 8.8 psi shear value is likely a surface effect due to the high crosslink density of the cured adhesive, in which case it may be possible to overcome by aiding the adhesive in wetting out the stainless steel. By optimizing both photoinitiator level and UV dose, the experienced formulator will be able to maximize adhesive performance.



**Figure 8.** Creep recovery results, 25°C, 2 psi.

## PSA Performance

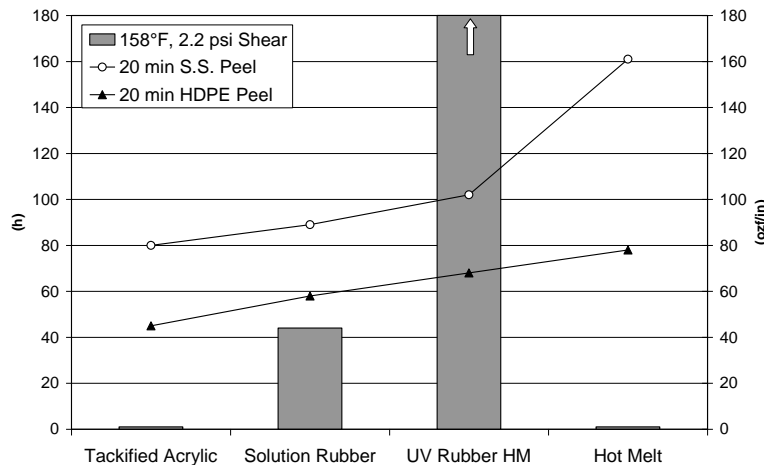
Once an optimized formulation and UV dose are chosen, we must examine the overall PSA properties of the new UV-curable adhesive. Table 1 lists performance properties for a prototype UV-curable hot melt PSA which was coated at 50 gsm, cured at 90 mJ/cm<sup>2</sup> of UV-C, and transferred to 2 mil PET, which was Corona-treated prior to lamination.

**Table 1.** PSA properties of a prototype UV-curable hot melt PSA.<sup>5</sup>

Peel from Stainless Steel	102 ozf/in
Peel from HDPE	68 ozf/in
Loop Tack	110 ozf/in
Shear (72°F, 8.8 psi)	26 h
Shear (158°F, 2.2 psi)	180 h
SAFT (on 2 mil PET, 2.2 psi)	240°F

The heat resistance and adhesion of the UV hot melt is compared to other PSA technologies in Figure 9. The tackified solution acrylic, the rubber-based hot melt for high heat applications and the solution rubber product are all commercial adhesives available from Henkel.

Once again the UV rubber-based hot melt exhibits higher heat resistance due to the covalent crosslinks formed through UV-curing. In this case we are measuring shear holding power at elevated temperature. The UV hot melt can withstand a 2.2 psi load at 158°F (70°C) for more than 1 week. Meanwhile, the solution rubber fails much more quickly and the tackified acrylic and standard hot melt fail immediately.



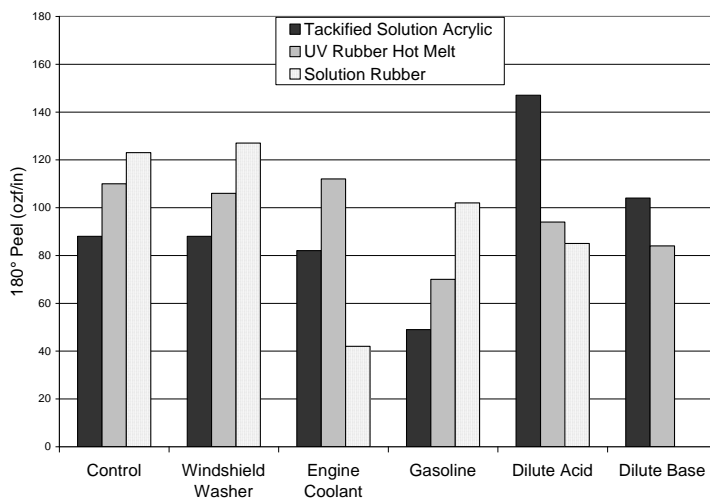
**Figure 9.** PSA properties across technologies, 50 gsm, transfer coated to 2 mil PET.<sup>5</sup>

As was stated earlier, an advantage of rubber-based PSAs is their high peel and tack. The UV-cured hot melt has slightly higher adhesion to both stainless steel and HDPE than the solution rubber and tackified acrylic, and has considerably higher peel than many acrylic PSAs. However, the UV HMPSA cannot achieve the same level of peel from stainless steel as the most aggressive hot melt PSAs, as such high values are achieved through cohesive failure whereas the highly crosslinked hot melt fails adhesively. Its peel force of 100 ozf/in is still well within the range of a good general purpose hot melt. With regards to tack, the UV rubber HM is again superior to the tackified acrylic and solution rubber products. Overall, UV-rubber hot melts offers a good balance of peel, tack and shear while providing exceptional heat resistance.

## Chemical and UV Exposure

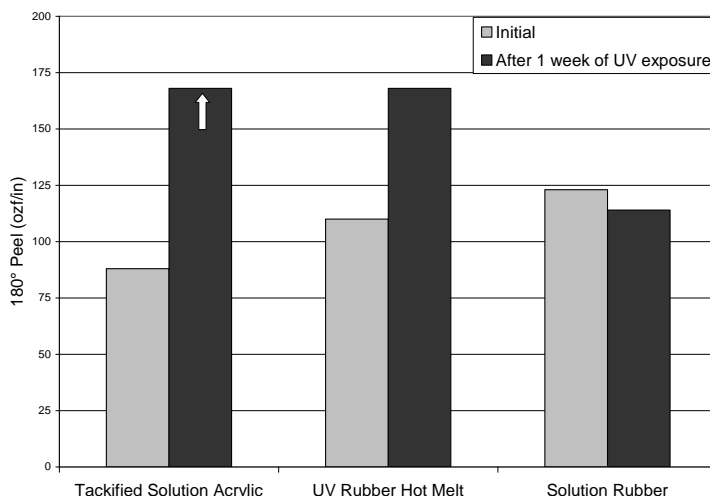
For more demanding industrial tape applications the adhesive must withstand exposure to a variety of chemicals and to UV light. It was predicted that the UV hot melt would perform similarly to the tackified acrylic due to its covalent crosslinks.

Chemical resistance data are shown in Figure 10 for a tackified acrylic, UV hot melt and solution rubber product. For this testing, 50 gsm films, backed with 2 mil PET, were bonded to stainless steel panels. The panels were then submerged in different test solutions for four hours. Finally a peel test was run to evaluate adhesion. The UV HMPSA performed similarly to the tackified acrylic in windshield washer fluid, engine coolant and gasoline, particularly when we looked at the percent change in peel values. In acid and base, the solution acrylic adhesive experienced an increase in peel as a result of cohesive failure. (This may be exaggerated somewhat since the control condition was a 20 minute peel, rather than a 4 hour peel.) The solution rubber adhesive performed very poorly in engine coolant and dilute base, where the strips fell off the panel. We can conclude that a UV-curable hot melt might be useful in applications where similar levels of chemical resistance are required.



**Figure 10.** Chemical resistance results.

It is also desirable for industrial tapes to retain their adhesion and maintain color upon exposure to UV light. Figure 11 shows peel adhesion before and after UV exposure. Tape samples were bonded to stainless steel panels, which were then placed in a QUV accelerated weathering tester using UV-A bulbs. An increase in adhesion was seen for both the UV rubber-based hot melt and the tackified solution acrylic, which experienced facestock failure.



**Figure 11.** UV aging results.

Additional tape samples were placed in the QUV to assess color change upon UV exposure. After two weeks in the chamber, there was no visible color change in any of these adhesives. Longer-term UV aging is underway. Overall, the UV HMPSA performed as well as the other adhesives upon UV aging.

## Conclusions

There are many photoinitiators on the market capable of crosslinking styrenic block copolymers. By utilizing a novel polymeric Type II photoinitiator, we can produce adhesives with reduced or zero extractable photochemicals and good thermal stability. These rubber-based UV-curable PSAs can be coated and cured at reasonable line speeds to make commercial tapes with good peel and tack performance and improved heat resistance. Promising chemical resistance and UV aging results open the door to new applications for hot melt adhesives.

## References

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