NEW RADIATION CURABLE ACRYLIC PSAs

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Radiation curable pressure sensitive adhesives are certainly not new. In fact, tapes have been produced from such adhesives for many years, most notably by captive manufacturers. Participation in radiation curing by the merchant tape market has historically been minimal, although an increased interest has been seen in recent years. This can be attributed in part to the rising prices of oil-based feed-stocks and their impact on the costs of solvent acrylic adhesives, as well as local environmental pressures in some cases, plus of course, the increase in availability of UV-curable adhesives.

The potential coating speed improvements offered by UV-cured adhesives, over solvent based systems, has also been an influencing factor on many adhesive manufacturer’s decision to examine UV curing as viable alternative to more traditional pressure sensitive adhesives. At National Adhesives we strongly believe that future growth and development of the pressure sensitive tape market is possible with this technology, despite the relative maturity of the sector today.

Much has been written about the potential for reduced cost-in-use for the tape maker using a radiation curable hot melt instead of a solvent-based acrylic PSA to produce a tape, therefore these cost comparisons will not form a major part of this paper. Instead, we will focus on our work to develop adhesives and technological approaches that are capable of delivering cost-effective, performance driven solutions targeted towards the production of industrial transfer tapes.

Why Focus on Transfer Tapes?

In selecting industrial transfer tapes as our initial development focus, we started by making a very simplistic segmentation of the pressure sensitive adhesives market into two basic categories – industrial tapes in all their many manifestations (transfer, double-coated, foam etc.) and graphics, with its many definitions (labels, decals, product branding etc.), as shown in Figure 1.

![Figure 1. Simple performance map.](image-url)
In general, the industrial tapes segment has higher cohesion requirements, and a broader spread of adhesion needs. When we then looked at many of the radiation curable PSAs available commercially today, including our own product offerings, we found that they generally failed to meet the more demanding needs of industrial tapes, as displayed in Figure 2.

![Diagram showing Peel and Shear for Industrial Tapes and Graphics with Current UV products highlighted.]

**Figure 2.** Current UV map.

For radiation curing to truly find utility in the pressure sensitive tape market, it has to meet the performance needs of industrial tapes.

We further narrowed our initial focus to transfer tapes as the products in the market today in this segment will often have some of the highest performance properties. If we can meet those, it should be relatively easy to alter our performance to meet the needs of other segments.

There is one other critical requirement of a transfer tape which has often proven problematic in a radiation cured system, and that is the need for both faces of the tape to have the same adhesion properties.

**Through-cure**

A solvent acrylic adhesive will often have a molecular weight around 500,000 Daltons and a low (perhaps 0.2% on a dry basis) level of added crosslinking agent. When such an adhesive is dried and cured to make a tape, both faces receive heat from the drier and the tape will cross-link evenly with relative ease. Consider now the differences that exist with a radiation curable adhesive. If it is supplied as a syrup, the molecular weight will be very low (a few thousand at most) with a significant amount of monomeric species present. A curing process is required to create a significant molecular weight build in addition to forming a crosslinked network. Alternatively - and in our opinion, preferentially - the adhesive is supplied as a hot melt system, with a preformed polymer of substantial molecular weight. This molecular weight is still significantly less than the solution acrylic, and so the resulting crosslink density will typically need to be higher in the radiation cured adhesive than the solvent-based systems if one hopes to achieve reasonable cohesive strength. Furthermore, the radiation will be incident from one side of the tape only. As it passes through the polymer system, some of the light will be absorbed by the photoactive species, to effect reaction, as well as by other absorbing moieties in the adhesive. Less light will therefore reach the bottom of the film than was incident on the top, which could result in a lower
crosslink density on the side of the tape away from the radiation source (the “dark” side) than on the side that was closer (the “light” side). This phenomenon is well understood and is described by Beer’s Law, various forms of which are shown in Figure 3, for an incident light of intensity $I_o$, an absorbed portion $I_a$ and a transmitted residual light of intensity $I$.

$$I_a = I_o - I$$

Figure 3. Expressions of Beer’s Law.

The overall absorbance of the film, $A$, will govern the rate at which the incident light is absorbed. As can be seen in Figure 4, this is an exponential relationship.

Figure 4. Absorbance, $A$ vs. $I_o/I_o$.

The effect that the absorbance, $A$, has on the amount of light that is absorbed can be calculated, independently of the thickness of the film. As can be seen from the examples in Table 1, lower absorbance values give rise to lesser differences from top to bottom. The reverse is true for high absorbance films.

Table 1. Example of absorbed light gradient.

<table>
<thead>
<tr>
<th>$I/I_o$ (%)</th>
<th>Throughout</th>
<th>Top 1%</th>
<th>Bottom 1%</th>
</tr>
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<tbody>
<tr>
<td>0.1</td>
<td>21</td>
<td>0.23</td>
<td>0.19</td>
</tr>
<tr>
<td>0.3</td>
<td>50</td>
<td>0.69</td>
<td>0.35</td>
</tr>
<tr>
<td>0.5</td>
<td>68</td>
<td>1.1</td>
<td>0.37</td>
</tr>
<tr>
<td>1.0</td>
<td>90</td>
<td>2.3</td>
<td>0.23</td>
</tr>
<tr>
<td>3.0</td>
<td>99.9</td>
<td>6.7</td>
<td>0.007</td>
</tr>
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Minimizing this effect however, is not an insignificant challenge. For a pressure sensitive adhesive to perform well as a transfer tape it needs to have equivalent performance on both faces. This could be achieved by using a film with very low overall absorbance. This is difficult to achieve with an acrylic polymer, due to their inherent low wavelength absorptions. In addition, if one used a low photoinitiator level to achieve a low overall absorbance, then it could be anticipated that a low number of crosslinking reactions would occur, which may not give rise to desirable tape properties. Higher absorbance will come from a greater concentration of UV-reactive species and can give rise to more crosslinking and generally better tapes, but at the cost of potential face-to-face differences in cure level.

In addition to depending on the chemical composition of the adhesive, absorbance levels also vary with the thickness of the coated film. Equivalent face-to-face curing of thick films (such as 5 mils or 125 gsm) is therefore an even more difficult and especially important challenge to address if radiation curing is going to find a useful home in the manufacture of industrial tapes.

**Choice of Curing System: Radical or Cationic?**

The work described here uses radical cure systems. Cationic curing systems are also a possibility and these remove some of the potential tape performance variation as the cure can be initiated by light and then continue for some hours (or days) after exposure. Cationic curing processes can however be quenched by atmospheric moisture, which can become a potential difficulty in tape production.

Radical cure offers “instantaneous” cure during exposure to the UV source, which is attractive for making a tape of reproducible, known properties. Our work on radical systems has taken several approaches to enhance its viability in production of industrial pressure sensitive tapes (PSTs).

We have been focused on polymeric adhesives (hot melts) in which primarily crosslinking occurs during cure, rather than molecular weight build. There are several well established reasons why this route is more appropriate for making industrial PSTs than a curable syrup-based adhesive.

**Designing the System**

As we started to design our UV adhesives, we made several key decisions. Firstly, we wanted to make our own polymers, using our own knowledge and experience in polymer design and synthesis. Making the polymers ourselves gives us complete control over every aspect of the polymer. We also chose to make acrylic polymers, as their properties were well accepted in high performance tape markets already. In addition, we sought to develop and use proprietary photoinitiators and monomers to help enhance our product performance, and draw on our extensive in-house hot melt formulating knowledge, where needed, to help us to tailor the product performance.

We set minimum performance targets for an industrial transfer tape, as outlined in Table 2, drawing from the performance of solvent acrylic adhesives we already sold into these markets, and from readily available industry data. In addition, we identified secondary performance characteristics of importance, such as good chemical, humidity and UV resistance of the tape, as well as the ability to be coated up to 125 gsm, or 5 mils, and produce a transfer tape with equivalent face-to-face performance.
Table 2. Minimum performance targets for transfer tape.

<table>
<thead>
<tr>
<th>Test Description</th>
<th>Target Value</th>
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<tbody>
<tr>
<td>Peel from stainless steel</td>
<td>≥ 70 ozf/in</td>
</tr>
<tr>
<td>Shear (72 °F, 4.4 psi)</td>
<td>≥ 168 h</td>
</tr>
<tr>
<td>Shear (158 °F, 2.2 psi)</td>
<td>≥ 10 h</td>
</tr>
<tr>
<td>S.A.F.T. (on 1 mil foil; 2.2 psi)</td>
<td>≥ 200 °F</td>
</tr>
<tr>
<td>Loop Tack</td>
<td>≥ 40 ozf/in</td>
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Designing the System: Spacers and Bound Photoinitiators
When designing a polymer-based UV curable adhesive a key decision is whether the photoinitiator (PI) will be added as a discrete molecular species or be bound into the polymer chain. We have chosen to bind our photoinitiators. Since such species are already part of the polymer, only one reaction is needed in order to create a crosslink between two polymer chains, compared to at least two reactions with an unbound photoinitiator. This increases the efficiency of the curing process and therefore the level of photoinitiator molecules that engage in crosslink formation instead of other potential side reactions.

The link between the polymer backbone and the photosensitive functionality is very important. A simple acrylated benzophenone (Figure 5, structure (i)) will give a polymer in which the photo-active group is held close to the polymer backbone. This relative lack of mobility will reduce the effective ability to produce crosslinks in the polymer network. Many people have already realized that a spacer unit, to separate the benzophenone from the polymer is important.5

![Figure 5. Functionalized benzophenones.](image)

Structures such as those shown above were reacted into model acrylic polymer systems and the resulting adhesive polymers were coated into films and cured with UV light. Crosslinking would be expected to take place using hydrogen abstraction from the side chain moieties from monomers such as 2-ethylhexyl acrylate, which was present in a significant amount in the polymer. We have examined various spacer units, such as the hydrocarbon system shown in Figure 5(ii) (commercially available from UCB) and the flexible siloxane, Figure 5(iii). We found that 5(ii) could give better performance, with gel fractions up to 49%, but that the siloxane was definitely superior, giving gel fractions up to 69%. Evenness of through-cure was examined by comparing the shear and heat resistance properties of tapes that were both transfer and direct coated.

We have found that higher PI levels give rise to less uniform cure through the film thickness, as discussed earlier. Lower levels were better for making transfer tapes with equivalent performance on both faces, but those tapes had a lower overall crosslinking level, and so were less suited to the
performance needs of industrial tapes. Their performance, in fact, was a potentially attractive match to the “graphics” performance window shown in Figure 1. The approach we have taken was ultimately more complex. We have found that careful optimization of both the photoinitiator level and type is needed, in addition to consideration of the composition and architecture of the polymer backbone. Through this combination approach we have been able to balance the properties of the tape with evenness of the through-cure.

We also examined various methods for enhancing the efficacy of the cure, such as “red-shifted” photoinitiators and photosensitization. This work however did not produce performance results beyond those which we have produced with bound benzophenones using carefully designed spacer groups.6

**Designing the System: Polymer Composition**

Having selected our photoinitiator system, we started to design our polymer systems. The model polymers we had used in the PI design, with compositions such as 80% 2-ethylhexyl acrylate and 20% methyl acrylate did not produce tapes with particularly high performance. Obviously we would have to employ functional monomers to enhance the performance. In solvented systems, by far the most common functional monomer is acrylic acid. This cannot be used at anything above very low levels in a hot melt system due to the extreme influence it has on the hot melt viscosity through hydrogen bonding. Many high performance tapes made from solvent rely on significant acrylic acid levels in the polymer to help achieve their performance. Since that was not a viable route here, we looked for other functional monomers.

Whilst the details of the monomers we choose are proprietary, the results and trends obtained are not. We found that we could exert significant control over the properties of the tape by adjusting the levels of functional monomer, such as the shear properties shown in Figure 6, measured on 50 gsm tapes that were transfer coated and cured with 50 mJ/cm² of UV-C radiation.

![Figure 6. Shear vs. functional monomer content.](image)

The choice of 50 mJ/cm² is not arbitrary. We have carried out extensive studies of the variation of tape performance with UV exposure in order to determine the exposure levels necessary for full cure and our findings in this area will be discussed later in this paper.
To date, we have achieved very encouraging tape performance with our designed polymer systems. This performance is summarized in Table 3, for 50 gsm transfer tapes on 2 mil PET backings. A look back at the targets we imposed on ourselves in Table 2 will show that have not quite met all of the goals and are certainly not exceeding them to any great extent. This in part reflects what others have also found – emulating the performance of a high molecular weight solution acrylic with a lower molecular weight UV-cured hot melt is not an easy task.

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These adhesives can be through-cured evenly to a thickness of approximately 100 gsm, or 4 mils. Whilst this falls short of our target of 125 gsm, it does represent the great majority of the tapes being produced from solvent today. In addition, with the correct lamp design and coating line set-up, these adhesives can be coated at 100 gsm at the same speed that would be used to coat them at 50 gsm – something that is certainly not true for solvent-based adhesives.

We have also closely studied molecular weight and its effect on properties. Obviously, a higher molecular weight gives better ultimate tape properties, but again there is a trade-off. Higher molecular weights become challenging to coat and process as hot melts. Extensive process development work on both polymer synthesis and solvent removal has ensured that our polymers can be reliably produced at their optimal molecular weight.

**Designing the System: Formulating Latitude**

To enhance our adhesive performance beyond what we had obtained so far with single polymer adhesives, we chose to look at formulation. Tackification is an obvious avenue of study, as are additional functional materials that may help to enhance the crosslinked network in the adhesive.

As the presence of non-functional formulating materials will effectively dilute the crosslink density and generally increase the UV absorbance, we had to design a formulating approach that would overcome this double effect. We have used two approaches: formulation with traditional tackifiers as well as relatively UV-transparent polymers, and selection of a slightly different design and level of photoinitiator. Together, these approaches are successful in leaving the through-cure properties of the tape unaffected, even in a highly formulated adhesive.

Some of the results of this dual approach are demonstrated in Figure 7. These results were obtained with 50 gsm transfer tapes and show a marked improvement in cohesion and through-cure over a more traditional tackification approach. The remaining results in this section all use polymers with the new photoinitiator design and level, formulated with this new approach.

The choice of a tackifier employed in our UV-curable adhesives is made more difficult by the fact that many acrylic-compatible resins have significant UV absorptions, which can readily create difficulties in
properly curing the adhesive. We have found some resins which we are able to use and still create fully cured adhesive tapes.

Figure 7. Cohesion variation with formulating approach.

Curing thicker tapes also becomes difficult with a formulated system, as the absorption values of the adhesive are still generally higher than before the polymer was formulated, despite efforts to use materials with minimal UV chromophores. Our techniques of using formulating agents which have relative UV-transparency, along with our ability to control PI structure and level certainly help us to maximize the efficiency of curing in thicker tapes. The overall level of tackifier employed still has limitations, just as it does in a solvent acrylic adhesive – more tackifier gives greater adhesion, to the detriment of cohesion, as demonstrated in Figure 8.

Figure 8. Performance variation with tackifier loading.
Performance Window

As a result of the various synthetic and formulatory approaches we have studied, we are now able to map out a performance window for our UV PSAs. As is shown in Figure 9, this window falls within our target performance area, and is suitable for use in industrial transfer tapes, having performance similar to some solution acrylic PSAs used in this area today. Significantly, this is something we have been previously unable to achieve with former approaches to making UV hot melt pressure sensitive adhesives. Although our understanding of the performance we can obtain is far from complete, we feel strongly that the performance can be further enhanced and developed towards specific applications.

![Figure 9. Performance map of new UV performance.](image)

Chemical Resistance and Aging Properties

It is obviously important for many industrial tape applications that the tape performs well in demanding environments, such as heat or chemical exposure. As these adhesives are based on covalently crosslinked acrylic polymers, they perform just as well as many solution acrylics would perform in these situations. Chemical resistance data for a prototype UV polymer is shown in Figure 10. The tests were performed by immersing 50 gsm tapes with PET backing, bonded to stainless steel panels, into the various test solutions for four hours and then measuring the bond strength. In most cases, the adhesion is relatively unchanged and very little degradation of the bond was observed.

A similar situation exists with heat and humidity aging of 50gsm tapes. Figure 11 shows the behavior of the same prototype adhesive when aged on stainless steel panels under various conditions for three weeks. Heat aging was carried out at 158°F; heat and humidity aging was carried out at 95°F and 95% relative humidity. Although some changes are observed, none of the samples displayed complete loss of adhesion or became brittle.
A frequently voiced concern of many people who are considering using UV curable adhesives is the potential for variation in tape properties if the UV exposure during coating should vary. This is a valid concern and can indeed be a problem, in just the same way that a variation in oven temperature could cause tape properties to vary when coating an adhesive from solvent.

We have studied the required UV exposure for our adhesives and have determined that all of the compositions discussed in this paper can be considered fully cured if they have a UV-C exposure of at least 1 mJ/cm² for each gram per square meter of adhesive coatweight. In other words, a 50 gsm, or 2 mil coating requires at least 50 mJ/cm² of UV-C exposure. Exposures above that level (within reason) do not cause problems or “over-curing” phenomena.
When examining peel adhesion, this is not readily obvious, as only a minor variation of performance with exposure is observed (Figure 12). In fact, peel varies more directly with coatweight, as would be both expected and typical for pressure sensitive adhesives. There is a noticeable increase in peel with increasing coatweight, and a relatively low dependence of peel on UV-C exposure.

![Figure 12](image.png)

**Figure 12.** Peel variation over a range of coatweight and UV exposure combinations.

A much more interesting and useful picture can be obtained by looking at cohesion values and their variation with coatweight and exposure (Figures 13 and 14). It is from these relationships that we have drawn our guideline of 1 mJ/cm² of UV-C per gram per square meter of adhesive.

Both the shear and S.A.F.T. values vary significantly if the UV-C exposure falls below the recommended levels. Operating in this region would readily produce tapes of variable performance. Any minor change in applied coatweight, line-speed or lamp power could result in different cohesion properties.

As the exposure increases however, it reaches a plateau above which the cohesive properties of the tape remain relatively constant when the exposure is further increased for any given coatweight. Running the coating operation above the onset of the plateau creates an operating window for the tape maker which will be accommodating to any minor exposure, line-speed or coatweight variations.

If a coater was equipped with three UV lights, arranged sequentially, each able to output 400 W/in of power, then a 50 gsm coating could be fully cured at 180 fpm. Similarly, a 100 gsm coating could be cured at 90 fpm.
Figure 13. 70°C Shear variation over a range of coatweight and UV exposure combinations.

Figure 14. S.A.F.T. variation over a range of coatweight and UV exposure combinations.
Conclusions and Forward Plans

This paper has addressed the development of UV curable PSAs for industrial tape applications. This of course is only the beginning. We believe that UV adhesives will form a viable long term option for the replacement of solution acrylic PSAs in many applications. This paper has also focused on only one type of curing chemistry (free radical) and one type of polymer (acrylic). We have studies in place to expand our portfolio into other end uses and other technological approaches.

For now however, we believe that UV curable PSAs most definitely have a future in the manufacture of pressure sensitive tapes. We are able to begin meeting the properties required for transfer tapes and we have developed an understanding of how to tailor and focus the performance of our polymers beyond the examples presented herein.

References

5. For examples, see:

Acknowledgements

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