Much has been written about the potential of radiation curing in the pressure sensitive adhesive industry in recent years: offers of improved performance and coating speed over current materials, along with less environmental concerns. Radiation curing remains, however, an art practiced largely by the captive tape market, with little to no involvement of the broader group of tape making companies.

Why is this? In part, the explanation is simply an inherent caution over entering a new technology, with unfamiliar equipment and materials. There are also many perceptions and unanswered questions about UV curing and its possible difficulties and downfalls. These often include concerns around the difficulty of controlling dose and the potential for a variable product if the dose is not constant as well as the difficulty of producing thick films for industrial tapes, due to limitations on the depth of cure. This paper will dispel many of those concerns and demonstrate that UV curing offers a broad platform of opportunities for the future of pressure sensitive tapes in many performance areas.

National Starch has a range of approaches to UV curing, many of which offer some unique ways of simplifying and removing the tape makers concerns. For convenience, UV curable systems can be split into three broad categories – first, second and third generations.

The first generation (Figure 1) consists of a monomer syrup approach. A combination of monomers – typically including some multi-functional monomers for crosslinking – and a photoinitiator are mixed and partially polymerized by thermal methods, to give a suitable viscosity syrup. This mixture is then coated onto the liner or substrate and cured, building the polymer system along the length of the coating line. Such an approach has been used to great effect by skilled manufacturers, but it is fraught with difficulties for the newcomer. Aside from the need to understand polymer composition and the effect of monomer choice on adhesive performance, the technique will run slowly and the line has to be fully enclosed and run under an inert atmosphere, which is a costly proposition. A low dose of long duration is needed in order to build sufficiently high molecular weight into the adhesive. The resulting tape may also have a significant level of residual monomer.

![Figure 1. First Generation](image-url)

The second generation approach, using oligomer syrups (Figure 2) is a technology widely used in the inks and coatings industry. Here, specially formulated syrups are used. These syrups contain a mixture of functional and non-functional oligomers along with monomers, multi-functional monomers and photoinitiators. A significant advantage of syrups over first generation systems is that they do not require inert operating conditions. However, they can be costly and are not always well suited to high-
performance pressure sensitive tapes. The low molecular weight oligomers are usually formed into a network with a relatively high crosslink density. Whilst this may work well for an ink or coating, it can cause fairly stiff materials with limited tack – less ideal for a tape.

The majority of work at National Starch has focussed on what we term third generation systems (Figure 3). Here, a 100% solids, or hot melt approach is used. The polymers are already formed and the UV curing process is used largely to add crosslinks to the adhesive. Third generation systems do not need inert conditions and have little to no residual monomer. There are also broad choices of formulating components and thus, many different tape performances can be created.

In the diagram above, X represents a reactive center, which could be a polymer-bound photoinitiator or a pendant functionality, capable of inducing crosslinking. If the photoinitiator were not bound to a polymeric component of the adhesive, then it would be added as a separate ingredient. For the tape maker, a third generation approach presents the easiest way to begin to work with UV curable adhesives.

**Figure 2.** Second Generation

**Figure 3.** Third Generation

Control of dose

With any radiation-cured adhesive, it is necessary to maintain a reasonable degree of control over dose. If the dose varies significantly between coating runs, then the end properties of the tape will obviously
be affected. In many respects, this is not different to the control needed over oven settings when drying and curing a solvated adhesive. There are many in-line monitoring and control devices that can be used to help simplify this process and make it as routine as running a drying oven.

**Radical cure**

There have been commercially available radical-cure PSAs for several years, although with limited market success. These systems are mostly based on acrylic polymers, often with bound photoinitiators. The photoinitiators used have significant absorption in the shorter wavelength regions of the UV spectrum, as does the acrylic polymer. This has limited the potential for these systems to be used in the production of high-performance pressure sensitive tapes, many of which may be coated at a thickness of 5 mil or more. The current design of many acrylic systems places limitations on uniform through cure at those tape thicknesses.

There are newer developments in acrylic systems using “red-shifted” photoinitiators (*i.e.* initiators with absorptions at longer wavelengths of the UV spectrum) which help with depth of cure. The longer wavelengths of light will penetrate deeper into the film. We have some significant developments of our own in this area, although they are beyond the scope of this paper.

**Cationic cure**

Cationic initiators have also played a significant role in expanding the possible depth of cure. Whilst some of these materials have red-shifted absorptions, the principal reason for their success in curing thick films is that the curing reaction continues beyond the duration of exposure to the light. This is in contrast to radical photoinitiators that will only form radicals and effect reaction while being exposed to the UV radiation.

The cationic process is initiated under the UV lamp (and may reach a significant extent), but the tape will continue to cure after exposure to the light, for up to several days. In fact, the same ultimate properties can be produced in tape samples that were given significantly different doses of light.

Two typical cationic initiator structures are shown in Figure 4. The materials are salts: in this case they are antimony salts. Phosphorous salts have also been used, although often less effectively. Obviously, there is still significant conjugation present, to create UV absorption.

![Figure 4. Cationic initiators](image-url)
On exposure to UV light, cationic initiators will form a strong acid (HX in Figure 5 below). This acid can then react with electron rich centers, such as oxygen atoms to create crosslinks and chain extensions. In the example mechanism below, the acid protonates an epoxide, which can then react with either an alcohol or another epoxide. If both of these functionalities are on polymer chains, then the reaction with an alcohol will join two chains together. A molecule of acid is also generated, which can induce another reaction. The reaction with the second epoxide is more significant for crosslinking. In this case, the product still contains a positive charge and so can go on to react with a third polymer chain.

\[
\begin{align*}
\text{HX} + \begin{array}{c}
\text{O} \\
R \quad R
\end{array} & \rightarrow \begin{array}{c}
\text{H} \\
R \quad R \quad O^+ \\
R \quad R
\end{array} + X^- \\
\text{HX} + \begin{array}{c}
\text{OH} \\
R \quad R \quad \text{OR'}
\end{array} & \rightarrow \begin{array}{c}
\text{OH} \\
R \quad R \quad \text{OR'}
\end{array}
\end{align*}
\]

**Figure 5.** Cationic cure mechanism

This chemistry is the basis of the cationic cure work at National Starch. We have used two materials from Kraton Polymers as the building blocks of our formulations.1 One is a poly(ethylene-butylene) polymer with a hydroxyl group at the chain end. The other polymer also has a poly(ethylene-butylene) portion, with a terminal hydroxyl group at one end, but it also has an epoxidized isoprene block at the other end, shown schematically in Figure 6.

**Figure 6.** Polymer structures

Through careful control of the ratio of these polymers (in particular, the ratio of epoxide to alcohol), and additional formulating ingredients, it has been possible to obtain some excellent pressure sensitive tape
performance. In these systems, the photoinitiator is not bound to the polymer but is dispersed through the adhesive.

We have repeatedly produced tapes up to 5 mil thick, with even and complete through-cure. A summary of the peel performance of two formulations, A and B, is shown below (Figure 7). Formulation A is a warm melt material, coatable at 200°F, whilst formulation B is a more viscous material, with a coating temperature of 250°F. Except where indicated, the examples discussed in this paper were cured with 220 mJ/cm² of UV-A, 200 mJ/cm² of UV-B and 30 mJ/cm² of UV-C, from a 400 W/in bulb operating at 50% power on a pilot coater running at 60 feet per minute.

![Figure 7. Peel performance](image)

As can be seen above, these two adhesives bond well to both steel and high-density polyethylene, which gives them many potential applications. In addition, all of the peels showed adhesive failure.

Obviously, for a high performing pressure sensitive tape, it is important to have good shear and heat resistance properties as well. Our cationic cure systems also display excellent properties in these areas.
The graph in Figure 8 below shows the shear adhesion failure temperatures (S.A.F.T.) of both materials at different thicknesses. These were measured at 2.2 psi (1” x 1” x 1 kg) on polyester backing. Formulation A does not fail by the end of the test, at 300°F, whilst formulation B, although it fails earlier, still shows good heat resistance.

![Graph showing shear adhesion failure temperatures (S.A.F.T.) for materials A and B at different thicknesses.](image)

**Figure 8.** Shear adhesion failure temperatures

This heat resistance is matched by the excellent shear performance of the adhesives. Both exhibit very high room temperature shear holding power when measured at 8.8 psi (0.5” wide x 1” high x 2 kg), as shown in Figure 9. Formulation A will hold for 12 to 30 hours, depending on the film thickness, and formulation B will hold for many days. The 2-mil film holds beyond the 140-hour level shown below, in fact, it will hold beyond one week.

![Graph showing 8.8 psi shear holding power for materials A and B at different thicknesses.](image)

**Figure 9.** 8.8 psi Shear

The shear and heat resistance of the adhesives is obviously due, in part, to the covalently crosslinked network created by the radiation curing. Covalent crosslinks will remain stable at higher temperatures than metal chelates, used to crosslink many solvent-borne acrylic pressure sensitive adhesives. This
stability is shown clearly in the dynamic mechanical analysis, in Figure 10. The modulus of both formulations remains flat and stable out to high temperatures.

Aging studies

Often, concern is expressed that UV cured adhesives will not age well under exposure to heat or sunlight – residual photoinitiator may result in further reaction and a change or loss of properties. A well-designed adhesive that has been properly cured will not exhibit any more degradation on aging than would be expected for the polymers involved. Both of the formulations described above age extremely well. Samples of 2 and 5 mil tapes made with the two adhesives were aged at both 200°F and 300°F, adhered to a steel panel as well as on liner. In all cases the performance remained unchanged after one month of aging and subsequent peel tests still showed adhesive failure.

The samples that were aged on liner showed little signs of color change or degradation, and they still exhibited peel strengths equivalent to material that had not been heat aged. The graphs below (Figure 11) show the peel performance from the samples that were adhered to panels and aged for up to 28 days at both 200°F and 300°F. The performance remains essentially unchanged for both adhesives at both 2 and 5 mil thickness. In addition, the color of the materials has not changed. Both have retained their very pale color throughout the test.

**Figure 10.** Dynamic mechanical analysis
There are obvious concerns over the performance of UV-cured adhesives when exposed to sunlight – after all, the adhesive cures by exposure to UV light, and there is UV radiation present in sunlight. We exposed our adhesives to UV irradiation in a Q-UV unit, fitted with UV-A bulbs, the most representative of sunlight. The samples, backed by polyester, were exposed to the bulbs through a polypropylene liner, which will absorb almost none of the light. After one month of exposure, the color of the samples was almost unchanged. We also exposed sample strips, backed by polyester and adhered to steel panels. Over the course of the month, the adhesive did not detach from the panel, although the polyester did become brittle, making peel measurements difficult.

**Chemical resistance**

We have also examined the chemical resistance of the adhesives, an important consideration for many industrial tape applications. Strips of tape were bonded to steel panels and immersed for four hours in 1M acetic acid, 1M sodium hydroxide, automotive antifreeze, automotive window cleaner or gasoline. After immersion, the panels were dried and the strips were peeled off. As can be seen from Figure 12,
in all cases except the gasoline immersion, the performance of the adhesive was unaffected. The peel values remained at the level obtained with strips that had not been immersed. There was no visible penetration of the test strips by the fluids. In contrast, the gasoline immersion values have dropped. In all cases, the gasoline had begun to penetrate the edges of the samples and had caused some debonding, of around 40 – 50% of the sample area. The portion of the adhesive that was not penetrated still gave adhesive failure when peeled.

![Figure 12. Chemical resistance](image)

“Dark-cure” and quality control

There is one common concern about a “dark-cure” system such as this. If the tape is not fully cured immediately after exposure to the light, then what methods can be used to check the quality of the tape and know that the final properties will be correct? Obviously, there is a need for a quality control test that can be performed as the coater is running and that can be calibrated to the performance of the tape after it has reached its ultimate cure. We have found that, when using the preferred dose, a significant quantity of cure is complete directly after exposure to the light. The development of peel strength with cure time is shown for 2 mil coating of Formulation B in Figure 13. The cure is largely complete after one day. This work was carried out using a dose of 140 mJ/cm² of UV-A, 120 mJ/cm² of UV-B and 20 mJ/cm² of UV-C, which is half of the dose previously quoted. Obviously, ultimate performance would be reached even more quickly with the higher dose.
This low-dose study also helps to demonstrate the relative insensitivity that these adhesives have towards dose. Despite using a significantly lower dose, the same ultimate tape properties can be obtained.

We have also developed similar cure profiles with other test properties, most usefully, dynamic shear. It is fairly straightforward to correlate a measurement made while the coater is still operating with the performance value that will be obtained when the cure is complete.

Moisture control during cure

From an examination of the cure mechanism presented in Figure 5, it will be obvious that water could also react with the cationic intermediates and inhibit the cationic propagation reaction. It is therefore important to control the level of moisture in the liner being used.

We have studied the level of cure obtained in Formulation A, coated on liners with various moisture levels, by using the S.A.F.T. and peel of the resulting tape as an indication of cure (Figure 14). If the moisture content of the liner is above 4%, then the S.A.F.T. of the tape begins to decrease significantly whilst the peel values increase, tending towards cohesive failure. This is clear evidence that the moisture in the liner is impacting the cure and producing a tape with a lower crosslink density.

It is therefore important to use liners with less than 4% moisture in order to obtain the optimal cure for these adhesives.
Conclusions

This work represents only one facet of the radiation curing studies at National Starch. As already indicated we also have ongoing research into radical-cure systems, acrylic systems and others. However, the chemistry discussed here presents a significant advance over many of the radiation-curable pressure sensitive adhesives available today, not only in their performance but also in their tolerance, ease of use and potential application to the production of high performance pressure sensitive tapes.

References


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Graeme A Roan received his Bachelor of Science degree in chemistry from the University of Strathclyde and his PhD from the University of Nottingham. He has worked in the ICI group since 1996, originally in the former ICI Acrylics business (now Lucite International) in both the UK and the USA before moving to National Starch in 2000. Since that time, he has worked in the Pressure Sensitive Adhesives business. He has been involved in a range of technology platforms, including 100% solids UV-curable materials. He also manages programs and develops acrylic and rubber-acrylic hybrid polymers and adhesives for solvent based systems.