Advances in Light Curing Adhesives and Coatings Lead to Process and Quality Benefits in Electronics Manufacturing

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Abstract
Radiation curing of adhesives and coatings continues to make technology advances. In particular, curing with light has seen many developments. Ultra violet curing technology has been enhanced by and is now allied with visible light curing. Visible light curing offers process improvements and advantages in health and safety. Synergistic use of UV and visible light gives better cure speeds and depths, and allows more applications, which were previously difficult or impossible. Light curing adhesives, coatings and encapsulants are being used in the electronics manufacturing industry with increasing frequency because their properties and process advantages are a good fit for the manufacturing requirements which are dictated by current industry drivers, such as miniaturisation, environmental and health & safety demands, manufacturing yield improvement and total product cost.

Introduction
A recent paper by this author concentrated on current case histories of radiation cure (photo cure) adhesives in this electronics manufacturing sector. This paper will concentrate on the recent developments which will shortly impact on or are recently introduced to the factory floor. Also, it will muse upon some future possibilities for the technology.

Industry Drivers
The increasing take up of photo cure adhesives by the electronics manufacturing industry may in part be explained by the general driving forces which prevail within it:

- Miniaturisation - electronic products are getting smaller and faster.
- Environmental demands - restrictions on volatile organic compounds which contribute towards the greenhouse effect and the discussions about lead replacement are instances of current issues. Companies have espoused the "green" ideal as an ethic.
- Health & safety - increased responsibilities on companies for the safety of both their work force, and also their customers, in the widest sense of that word.
- Manufacturing yield improvement - high yields are achieved in electronics manufacture (6 sigma plus). The drive is to ensure that this level is routine. New technologies demand this because, for example, inspection and rework processes can become expensive or impossible.
- Total product cost - to achieve cost improvements, it is important to examine the entire process or product. A new element which is in itself more expensive may have process or performance implications which reduce the total product cost.
- Materials - the emphasis may be swinging from reliability to process-ability. This is not to imply that reliability is not important, or even not paramount. But the need to fit materials into a modern production environment with JIT philosophies means that their processing must be simple and consistent.
Design for manufacture - in the quest for high functionality, performance and appealing appearance, do not forget that someone has to produce it.

A Fundamental Change
In addition to these drivers, electronics manufacturing is undergoing a fundamental shift; it is changing from assembly to process. The assembly line introduced at Ford Motor Company in October 1913 reduced the time required to assemble an automobile from 12.5 hours to 1.5 hours, and revolutionised industry. We can still compare in our minds an electronics manufacturing factory with a car assembly line, with the addition of components and parts as the product trundles along some form of conveyor. But with increasing automation, and higher component functionality and more complex integration, the emphasis must be changing towards process, from assembly. A process line, where a series of operations are performed on the product, is the new paradigm.
Attention is focused on these processes, then, with the objective of minimising defects, down time, work in progress and response time.

Light or Photo Curing

The Electromagnetic Spectrum
Figure 1 depicts the electromagnetic spectrum, and highlights the optical region which runs from about 200nm to 400nm for ultraviolet light, and about 400nm to 760nm for visible light.
We are very familiar with the concept of the conversion of light energy into chemical energy. Photosynthesis is the process by which chlorophyll-containing organisms (green plants, algae, and some bacteria) capture energy in the form of light and convert it to chemical energy. Virtually all the energy available for life in the earth's biosphere is made available through photosynthesis.
We can also use light energy to change a "liquid" adhesive or coating into a "solid"; we call this light or photo curing or polymerisation.
Because of the inherent cost savings possible in faster cure, the technology of cross-linking polymers using photo-initiators which are sensitive to UV light has been the subject of research dating back to the 1950's. In the early 1980's, structural strength UV curing aerobic acrylic adhesives were introduced, and in the late 1980's, electronic grade versions were developed which are 100% solids, fast curing and can be used as adhesives or coatings.

Figure 1 - The Electromagnetic Spectrum
UV Cured Adhesives and Coatings
For electronics applications, the systems are primarily based on acrylic and urethane chemistries (although light curing epoxies and silicones are known).

In simple terms, these materials consist of monomers and oligomers, various agents and modifiers (e.g. wetting agents, stabilisers, fillers) and photo-initiators (Figure 2.1). These elements coexist without reacting with each other, until exposed to light of the correct wavelength and intensity. Then, the photo-initiators undergo a cleavage (Figure 2.2) and generate highly energetic species called "free radicals", which initiate the formation of monomer chains (Figure 2.3). After many propagation steps, the cross linked polymer chains are fully reacted, or cured (Figure 2.4)

The light curing process is very fast with the cure being affected in many cases almost instantaneously.

Figure 2 - The Free Radical Light Curing Process

General Features and Benefits of Light Curing Adhesives and Coatings
- Very fast cure - often in a second or two, instant
- 100% solids - solvent free
- Room temperature storage - no refrigeration
- Unlimited pot life
- Long shelf life - usually one year
- Single part - no mixing
- Ambient temperature cure
- Demand cure
- Low energy cure
- Available in wide range of viscosity
- Good thermal and moisture resistance
- Cured grades from flexible to hard
- Low toxicity with little or no odour
- Good adhesion to a wide range of substrates
- Will not bond skin
- Adapts easily to automated application
Electronics Applications

Since the late 80’s, hundreds of successful applications have been found for this technology. Use has been found in the electronics manufacturing industry in the following areas:

- Strain relief
- Wire and parts tacking
- Coil terminating
- Tamper-proofing
- Structural bonding
- Temporary masking
- Potting
- Encapsulation, glob topping, underfill
- Conformal coating
- Surface mount component attachment

Examination of a few case histories will demonstrate both the efficacy and the economics of using light curing adhesives and coatings.

UV Light Curing

Until recently, most light curing adhesives used in industry have been cured with ultra violet light. Historically, the first UV inks and coatings were “dried” with shortwave UV light in the 250nm range. These short wavelengths (UV-C) are hazardous; indeed, shortwave UV radiation can be used for sterilisation. Applications are restricted to well-shielded conveyorised systems.

The first true structural UV cured adhesives used longwave UV light (“black light”). Lamps used for curing generate peak intensities at about 365nm, and the photo-initiators used in the formulations react strongly in this range (Figure 3). Lamps can be filtered to exclude the hazardous short and medium wavelength UV light (UV-C and UV-B), leaving longwave UV (UV-A) and visible light only. UV-A is considered safe, and benchtop lamps have been developed which can be used with minimal precautions (e.g. eye protection).

Figure 3 - Relative Spectral Output of Curing Lamp
Cure Depth & Technology Restrictions
Light absorption by any material varies with wavelength. Short wavelength UV will be absorbed at the very surface of the material, and thus is restricted to UV "drying" very thin layers (inks and coatings). Because it is absorbed less well, longwave UV penetrates further. The first UV cure aerobic acrylic adhesives used longwave UV to cure, and were thus able to succeed in applications such as structural bonding, sealing and coating where cure depths could achieve up to 6-8mm. Certain plastics do not transmit UV light very well, if at all. Some have UV blocking agents which are added to prevent UV light ageing. Light curing technology would not work with many translucent, coloured or UV blocked substrates. Adhesive applications were restricted to shallow potting, sealing, bridge bonding or tacking applications where the adhesive is directly exposed to light. Potting and encapsulation was limited to transparent resins or thin layers of pigmented resins.

Visible Light Curing
New formulations have added a visible light cure in addition to the ultra violet, extending the light range usable by the adhesive up to about the 500nm level. This has given the technology of curing with light a number of very important advantages over traditional UV curing.

Cure Speed
Advocates of photo cure technology are already benefiting from cure speeds of seconds compared to minutes or hours for heat cure resins or solvent evaporation systems. The synergistic use of both longwave UV and visible photo-catalysts in adhesive formulations typically yields cure speeds up to 50% faster than formulations which cure only by absorbed UV light.

<table>
<thead>
<tr>
<th>Peak wavelength</th>
<th>Long Wave UV &quot;Black Light&quot;</th>
<th>Visible Light</th>
<th>Combined UV and Visible Light</th>
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<tr>
<td>365 nm</td>
<td>50 mW/cm²</td>
<td>-</td>
<td>50 mW/cm²</td>
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<tr>
<td>405 nm</td>
<td>5 mW/cm²</td>
<td>20 mW/cm²</td>
<td>20 mW/cm²</td>
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<tr>
<td>436 nm</td>
<td>-</td>
<td>25 mW/cm²</td>
<td>25 mW/cm²</td>
</tr>
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<td>Available energy</td>
<td>55 mW/cm²</td>
<td>45 mW/cm²</td>
<td>95 mW/cm²</td>
</tr>
<tr>
<td>Typical cure speed of UV only adhesive</td>
<td>10 sec</td>
<td>-</td>
<td>5 sec</td>
</tr>
<tr>
<td>Typical cure speed of UV/visible adhesive</td>
<td>5 sec</td>
<td>20 sec</td>
<td>2 sec</td>
</tr>
</tbody>
</table>

Table 1 - Typical Adhesive Cure Response to Various Wavelength Combinations
Table 1 shows the results of curing a traditional UV light cure adhesive and a new UV/visible light cure adhesive with a) only longwave UV, b) only visible light and c) a combination of the two. The first thing to notice is that visible light cure on its own is quite slow. For this reason, pure visible light curing adhesives have been used sparingly in industry to date, their utilisation being restricted to areas such as dentistry.

By extending the range of useful light wavelengths, we can increase the available energy to be used for cure. This, combined with the synergistic nature of the UV/visible cure combination, results in the fastest cure speed. Providentially, most curing lamps which are designed to be used with
longwave UV curing adhesives emit appreciable visible light; users can take advantage of this new technology without having to invest in new equipment.

**Cure Depth**
Curing with UV on thick materials can result in a cure gradient (the material on top is cured better than the material at the bottom). By using a UV/visible adhesive or potting compound, we can achieve greater and more consistent cure depths.

**Figure 4**
Absorption of light by an adhesive without photo-initiators (left axis). The strong absorption of shortwave UV radiation by the adhesive prevents the shortwave UV from penetrating into the adhesive. Visible light (>400nm) and longwave UV (>350nm) radiation penetrate further and provide better depth of cure (right axis).

**Light Transmission**
By adding the visible light curing photo-catalysts to the formulations, the range of materials which can be bonded, sealed or potted increases substantially. In the electronics industry, materials which could now transmit sufficient curing light include:

- Ceramics - hybrid circuit substrates, fibre optic ferrules
- Polyimide films - flexible circuits
- UV opaque plastics - relay bodies, connectors
- Translucent plastics
- Crystals and glasses

Any material which can be seen through is now a candidate for use in a photo cure adhesive application.

**Safer Curing Lamps**
In certain circumstances, we might now use just the visible light curing element of these new formulations. The enhanced cure speed of the UV/visible adhesives and coatings achieved with conventional curing lamps would be sacrificed to provide another advantage - protection from any UV.
Curing lamps are now available which output only intense "blue light", around the 420nm range. These could be used when sensitive substrates are being bonded or coated, for example some plastics which would quickly degrade under UV light, or circuitry which is optically delicate. Occasionally, conventional UV curing lamps cannot be used safely, or are perceived to be unsafe, in an application. This is despite the fact that, with appropriate safety wear (eye protection, gloves), it has been shown that operators' exposure to UV radiation from bench top curing lamps is well within safety limits and is harmless. Often these lamps are filtered to produce only safe, longwave UV-A. However, in these instances, a low intensity "black light" inspection lamp or a high intensity visible light lamp may be used for curing.

Filled Adhesives and Coating

With the additional penetration afforded by the use of a UV/visible light cure mechanism, adhesives and coatings may be formulated to contain some filler and still achieve good cure speeds and depths curing with light alone. Thickness of cured material will depend on bond geometry, intensity of light used and transmission characteristics of the fillers. Examples of fillers are borosilicate glass or alumina. Desirable enhanced properties of these filled adhesives or coatings are:

- Very low shrinkage - for precision bonding
- Thermal conductivity - heat sink attachment
- Electrical conductivity
- Opacity - security, cosmetics

Practical Considerations

Ambient light found in factories or outdoors in sunlight will eventually cure UV/visible light systems, but the light intensity required to quickly cure UV/visible light systems is much higher. While sensitive to light in the visible spectrum, the systems have very long open pot lives, and will stay in their "liquid" state until exposed to intense light, and then cure very quickly. Thus, they retain the very desirable "demand" cure property of UV cured systems. In the correct packaging which blocks 100% of both UV and visible light, the materials have very good packaging stability, usually in excess of twelve months at ambient storage temperature.

Secondary Cure Mechanisms

Even with the improved speeds and depths of cure given by combined UV/visible systems, full cure by light alone may not be possible in every application. Shadowing caused by component geometry (or adhesive fillers) may not allow even penetrative visible light to reach all areas of the adhesive or coating. Generally speaking, light curing adhesives and coatings will start cross-linking when the light is shone upon them, and stop almost immediately when the light is taken away. There is little or no proliferation of the cure into areas which are shielded from the light. As an aside, this phenomena means improved product stability on the shelf. When there are shadowed areas, a secondary cure mechanism can be employed to complete the cure. Anaerobic acrylic systems have been formulated with a number of these mechanisms:

- Activator - usually used when part of the bond is interfacial. A thin film of activator is applied to one surface, and bead of adhesive to the other. The parts are placed together. Fixture strength is achieved in less than one minute. Squeezed out fillets of adhesive and the balance of the material which is not interfacial may be cured very quickly with light.
- Heat - a 110ºC activation temperature can be used to complete the cure
- Atmospheric oxygen\(^8\) - UV cure, followed by polymerisation initiated in air similar to the reaction which converts an oil-based paint to a finished hard coating. Used in conformal coating applications.
- Two part mix\(^9\) - again used in conformal coatings. A wide tolerance "spray together" two part system is applied and UV cured. Shadow curing is completed at room temperature in up to one hour.

**Microelectronic Encapsulation**

The advantages of a combination of UV/visible light curing with a secondary heat (IR) cure mechanism has led to new applications in the microelectronics industry, specifically encapsulation or glob topping. Historically, high purity liquid encapsulants have been of epoxy or silicone types, which require thermal cures, often for hours at temperatures up to 150ºC.

Aerobic urethane encapsulants have been developed which have a combination UV/visible/IR cure mechanism.\(^{10}\) A special curing system combines UV and visible light to cure a thick, tough skin over the surface of the encapsulant. Photo curing occurs in seconds. Then, infrared heat cures any portion of the adhesive which was shielded or not directly exposed to the light. This may be under the die edges for COB or underneath a flip chip while underfilling. The heat cure only takes a minute or two. By virtue of the same combination of UV/visible/IR cures, opaque black encapsulants or glob tops with total cure times of a few minutes are available. Figure 5 shows how the deep visible light cure quickly provides a skin which allows the heat cure to be affected without "popcorning".

![Figure 5](image)

*Figure 5 - Combining UV and visible light for opaque encapsulant cure allows secondary heat cure with no surface eruptions or ripples.*

In addition to the process advantages of very rapid cure, photo cure aerobic urethane encapsulants have low modulus and low Tg. The resins’ innate flexibility and lack of fillers help reduce stress on sensitive segments of microelectronic assemblies like bonding wires.
New Applications
These are potential or actual applications which demonstrate some of the new uses for which photo cure adhesives and coatings (with some of their unique properties) are being considered.

SMT Component Bonding for Stress Relief
Bonding components to printed circuit boards to add structural strength during mechanical vibration and temperature cycling is a well-known and practised technique. Light curing adhesives have been shown to be ideal for this, even in military environments.\textsuperscript{11}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{tsop.png}
\caption{TSOP surface mount components, Type I and Type II}
\end{figure}

There have been reported problems with certain surface mount components which employ Alloy 42 lead frames, specifically TSOPs. Solder joint failures and cracking have been found during thermal excursions. The devices are often mounted on FR-4 printed circuit boards. The Alloy 42 leads are stiff compared to, say, copper, and the TSOP leads are short. If more than optimal solder is used, then excess solder will also stiffen the leads. With a CTE mismatch between the component and pcb, and little stress relief in the short, stiff leads, joint cracking can occur.

Solutions range from optimising the amount of solder in the joint to changing the pcb substrate material to ease the CTE mismatch. Another approach is to encapsulate the leads or underfill the device with a resilient adhesive in order to provide stress relief. In these cases, single part, UV/visible/IR aerobic urethane low modulus microelectronic encapsulants provide simple, fast and economic processing. Their high tensile strength combined with resiliency and elongation absorbs thermal stresses. Unlike brittle materials (e.g. epoxies), the high elongation urethane backbone acts like a shock absorber to reduce stress, and to dissipate both mechanical and thermal shock.\textsuperscript{12}

SMT Component Encapsulation for Security
Sometimes, components need to be protected for security reasons. For example, devices which contain electronic access codes may need to be coated so that it is difficult to electronically probe the leads and determine what the codes are (examples are mobile telephones and satellite TV decoders), or to prevent other forms of reverse engineering. In these cases, only the leads need to be encapsulated. The encapsulant will need to resist all but the most determined pirate, and so it will need to be resistant to any solvent or acid which the pcb itself could withstand (i.e. anything which dissolves the encapsulant will also dissolve the assembly), any mechanical attack which would remove the encapsulant but leave the leads extant, and soldering iron heat.
As in the previous example, it is important not to compromise the fatigue life of the solder joints by having a high modulus encapsulation material which might constrain the movement of the gull wing leads and puts added stress on the solder joints during temperature changes. A suitable encapsulant would have the following features:

- Single part, photo cure - for simple (robotic) dispensing and fast cure
- Very good adhesion to the component leads and body and the pcb itself - note that component bodies often have release agent residues on them, and may be difficult to bond to
- The correct viscosity which allows flow around the leads - but does not flow to unwanted areas, or underneath the device
- Resiliency - so as not to add stress to the solder joints during thermal excursions

**Flip Chip Bonding**

In flip chip technology, bare silicon chips are bumped with various tin/lead alloys or conductive polymers, placed face down onto the circuit substrate, and then soldered or glued with conductive adhesive. Whilst solder has been the dominant technique to date, the use of the adhesive technique may acquire greater importance if lead is banned from electronic production or drastically taxed for environmental reasons. Also, low temperature cure and therefore low thermal stress is an advantage of adhesive over solder.

However, placement accuracy will need to be higher than if solder attachment is used, as there is no self-alignment. Flip chips are very light, and so conductive adhesives with very high green strengths will be needed if the chips are not to be dislodged whilst moving through the balance of the pick and place system and on to cure.

It has been hypothesised that a light curing conductive adhesive will be used. The flip chip will be placed onto the substrate which has already had adhesive applied, by screen printing, dispensing or pin transfer. Whilst the placement head is still holding the part in the correct location (and perhaps adding some pressure to enhance conductivity), the adhesive will be photo cured with light from the sides of the device, and potentially through the substrate from the bottom. Enough fixture strength will be achieved to allow the assembly to move to a complete, probably heat, cure without risk of the chip moving.

UV curing conductive adhesives are already used for chip-on-glass applications. The addition of visible light to the cure process may allow this technique to be used more widely and on other substrates.
References


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