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UV and Thermal Cure Epoxy Adhesives

Chunfu Chen, Bin Li, Chao Wang, Shuichi Iwasaki, Masao Kanari and Daoqiang Lu

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Abstract

Typical commercial UV and thermal cure epoxy adhesives have been reviewed and compared. UV cure cationic epoxy adhesives are primarily composed of cycloaliphatic epoxy resin and cationic photoinitiator. UV cationic epoxy adhesives have no surface cure issue and possess low cure shrinkage and good adhesion performance but need post-thermal cure to achieve full adhesion performance in use. Hybrid UV acrylate and thermal cure epoxy adhesives are primarily composed of acrylate monomer, free radical photoinitiator, epoxy resin and curing agent. The hybrid epoxy adhesives combine fast UV curability of acrylate composition and high adhesion performance of thermal cure epoxy composition. A new type initiator free hybrid one-component UV and thermal cure adhesive has been also introduced. It is mainly composed of maleimide compound, acrylic monomer, partially acrylated epoxy resin, epoxy resin and latent curing agent. Its UV cure and thermal cure behaviour have been studied by FT-IR spectroscopy measurement.

Keywords: UV cure, thermal cure, cationic, free radical, acrylate, epoxy adhesive

1. Introduction

Epoxy adhesives are widely used in structural bonding applications ranging from general industry, semiconductor packaging, electronics assembly and automobile production to aerospace market because of their strong chemical structure and good adhesion to various substrates [1–9]. Epoxy adhesives are primarily composed of epoxy resin and curing agent. Figure 1 illustrates chemical structure and key features of various functional groups for bisphenol A diglycidyl ether, the most standard epoxy resin used in epoxy adhesives. Epoxide possesses high reactivity. It can react with amines, thiols, anhydrides or phenols almost equivalently via polyaddition mechanism at suitable certain conditions to become strong cross-linked thermoset
resins. As shown in Scheme 1 [10], epoxide reacts almost equivalently with active hydrogen in amine curing agent via polyaddition mechanism. Epoxide can also polymerize via either anionic or cationic polymerization mechanism. As shown in Scheme 2 [11], epoxide can polymerize via anionic polymerization mechanism initiated by anionic ion resulted from reaction of imidazole compound and epoxide. Epoxy adhesives can be cured at different temperature conditions based mainly on the curing agent type used but will normally need relatively long cure time ranging from half hour to a few days. Aliphatic amine-based epoxy adhesives, the most commonly used type, start to cure at room temperature. Thiol-based epoxy adhesives, the fastest cure type, start to cure even at low refrigerator temperature. Anhydrate-, phenol-, aromatic amine- or catalyst-based epoxy adhesives will normally need elevated temperature to achieve full cure. Generally speaking, epoxy adhesives designed to cure at elevated temperature which are commonly called as thermal cure epoxy adhesives have higher degree of cross-linking structure and glass transition temperature and thus show better performance than epoxy adhesives designed for cure at room temperature. Thermal cure epoxy adhesives can be also formulated as one-component type by the use of latent curing agents for easy handling. One-component thermal cure epoxy adhesives have been increasingly used in various applications such as semiconductor packaging, electronics assembly and automobile production where high production efficiency and high adhesion performance are required. Recently, UV and thermal cure epoxy adhesives have been

Figure 1. Structure and key features of bisphenol A diglycidyl ether.

Scheme 1. Polyaddition reaction of epoxy resin with amine curing agent.
developed and commercialized to meet further higher production efficiency of required applications such as precise optical sensor packaging and display assembly [12–15].

There are mainly two types of commercial UV and thermal cure epoxy adhesives: UV cure cationic epoxy adhesives and hybrid UV acrylate and thermal cure epoxy adhesives. UV cationic cure epoxy adhesives are primarily composed of cycloaliphatic epoxy resin and cationic photoinitiator. UV cationic epoxy adhesives have no surface cure issue and possess low cure shrinkage and good adhesion performance but need post-thermal cure to achieve full cure. Hybrid UV acrylate and thermal cure epoxy adhesives are primarily composed of acrylate monomer, free radical photoinitiator, epoxy resin and curing agent. The hybrid epoxy adhesives combine fast UV curability of acrylate composition and high adhesion performance of thermal cure epoxy composition.

2. UV cationic epoxy adhesives

UV cationic epoxy adhesives are primarily composed of epoxy resin and cationic photoinitiator [16–20]. Cycloaliphatic-type epoxy resins are usually selected for UV cationic epoxy adhesives because of faster cationic polymerization rate than that of normal bisphenol A diglycidyl ether-type epoxy resin. Chemical structure of typical commercially available epoxy resins suitable for cationic epoxy adhesives is shown in Figure 2. Cationic photoinitiator is the key raw material to formulate UV cationic epoxy adhesives. There are mainly two types of cationic photoinitiators: Bronsted acid and Lewis acid generator. Sulfonium and iodonium salts that can generate Bronsted acid are most commonly used as cationic photoinitiator. Figure 3 shows chemical structure of typical commercially available cationic photoinitiators.

As illustrated in Scheme 3 [21], photoinitiator in UV epoxy adhesives absorbs UV energy to generate strong acid that will react with epoxy to produce cationic which can initiate homo-polymerization of epoxy resin. UV cationic epoxy adhesives will need some longer cure...
Figure 2. Common commercially available epoxy resins for cationic epoxy adhesives.

3, 4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate

bis(3,4-epoxycyclohexylmethyl) adipate

Figure 3. Chemical structure of common UV cationic photoinitiator.

mixed triarylsulfonium hexafluoroantimonate salts

(4-Methylphenyl) [4-(2-methylpropyl) phenyl] iodonium hexafluorophosphate
time compared to UV cure acrylate-based adhesive. In actual use, a post-thermal cure of UV cationic epoxy adhesives after the UV radiation is commonly used for full cure to assure satisfactory adhesion performance. Compared to common acrylate-based UV adhesives, UV cationic epoxy adhesives have much lower cure shrinkage because of the epoxy structure and have no surface cure issue that is resulted from oxygen inhibition to free radical polymerization since they cure via cationic polymerization. By contrast, UV cationic epoxy adhesives are not suitable for alkali-type substrates which stop cationic polymerization.

UV cationic epoxy adhesives have been commercialized and used in optical parts bonding, sensor packaging and display panel assembly applications [22–26]. The authors have found that adhesion reliability performance of UV cationic epoxy adhesives can be much improved by the combination use of cationic photoinitiator with thermal cationic initiator [27].

3. Hybrid UV acrylate and thermal cure epoxy adhesives

Most widely used UV cure adhesives are acrylate-based compositions [28–32]. Acrylate-based UV cure adhesives are primarily composed of acrylate monomer, acrylate oligomer and photoinitiator. As shown in Scheme 4 [33], the photoinitiator formulated in an acrylate-based adhesive absorbs light energy via UV radiation to generate free radical which can rapidly initiate polymerization of acrylate compositions. Acrylate-based UV cure adhesives can be cured within seconds. Limitations of UV cure acrylate-based adhesives are the surface cure issue, shadow cure problem, high cure shrinkage and poor humidity reliability. Surface cure issue is resulted from oxygen inhibition to free radical polymerization of acrylate. Shadow cure problem always occurs at the area where light cannot approach. Relatively high cure shrinkage and poor humidity reliability are caused from acrylate chemical structure.
By the combination of UV acrylate composition with thermal cure epoxy composition, UV and thermal cure hybrid epoxy adhesives have been developed and commercialized for over two decades [34–38]. Acrylate monomer, epoxy resin, photoinitiator and epoxy curing agent are at least contained in the UV and thermal cure hybrid adhesives. These hybrid adhesives combine advantages from both UV acrylate proportion and thermal cure epoxy part. Adhesion reliability

![Scheme 4. UV cure mechanism of free radical polymerization of acrylate adhesives.](image)

<table>
<thead>
<tr>
<th>Adhesive type</th>
<th>UV acrylate</th>
<th>UV cationic epoxy</th>
<th>Hybrid thermal cure epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Key compositions</td>
<td>Acrylate</td>
<td>Epoxy resin</td>
<td>Acrylate</td>
</tr>
<tr>
<td></td>
<td>Photoinitiator</td>
<td>Cationic photoinitiator</td>
<td>Photoinitiator</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Epoxy resin</td>
<td>Epoxy resin</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Curing agent</td>
</tr>
<tr>
<td>Polymerization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UV cure</td>
<td>Radical</td>
<td>Cationic</td>
<td>Radical</td>
</tr>
<tr>
<td>Thermal cure</td>
<td>NA</td>
<td>Cationic</td>
<td>Polyaddition, anionic</td>
</tr>
<tr>
<td>Oxygen inhibition</td>
<td>Yes</td>
<td>No</td>
<td>Partially</td>
</tr>
<tr>
<td>Alkali inhibition</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>UV curability</td>
<td>High</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Post-thermal cure</td>
<td>No need</td>
<td>Preferred</td>
<td>Need</td>
</tr>
<tr>
<td>Shadow cure</td>
<td>No</td>
<td>Partially</td>
<td>Yes</td>
</tr>
<tr>
<td>Cure shrinkage</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Adhesion</td>
<td>Moderate</td>
<td>Good</td>
<td>Good</td>
</tr>
</tbody>
</table>

**Table 1.** Comparison of UV acrylate, cationic epoxy and hybrid thermal cure epoxy.
performance could be much improved by the introduction of the epoxy composition compared to the normal acrylate composition. In the meantime, production efficiency could be much improved by shortening the fixture time to seconds via UV cure compared to at least dozens of minutes needed for thermal cure epoxy adhesives. Surface cure issue, shadow cure issue and high cure shrinkage of acrylate-based UV adhesives could also be improved to certain degree because of lower contents of free radical curable acrylate compositions. In some cases, a thermal initiator such as peroxide is also formulated in the hybrid adhesive to assure curing remained acrylate compositions after the UV radiation or those at shadow area. Advantages and limitations of UV cationic epoxy adhesives, hybrid UV acrylate and thermal cure epoxy adhesives are compared with those of UV acrylate adhesives in Table 1.

4. Initiator free hybrid epoxy adhesives

Photoinitiator is the key material to formulate UV cure compositions. In actual cure process, however, several small molecules are usually generated as byproducts. Additionally, photoinitiator itself will not be consumed completely in actual use at most cure conditions and will remain in the cured materials as just contaminants. As shown in Scheme 5, for the use of benzyl dimethyl ketal (BDMK) as photoinitiator, for example, Sitmann et al. [39] described that there are at least three small molecules generated during its UV light decomposition. These small molecular byproducts, together with the remained photoinitiator, cannot be chemically bonded to the cured adhesive. For sensitive high precise substrate bonding applications such as fine semiconductor packaging or display assembly, there are big concerns on contaminants from low molecule chemicals such as these byproducts, remained photoinitiator during UV curing process on sensitive semiconductor substrate or display materials. In addition, the remained photo-initiator

![Scheme 5. Photo-reaction mechanism of BMDK.](http://dx.doi.org/10.5772/intechopen.82168)
may initiate or accelerate chemical reaction of cured adhesive materials during the actual use and potentially damage its adhesion reliability performance. Initiator free UV cure adhesive will not have these concerns.

Recently, the authors invented and reported a new type high-performance UV and thermal curable hybrid epoxy adhesive that is completely an initiator free composition but still possesses good UV curability and satisfactory thermal curability, suitable for use in high-end display assembly applications [40–42].

Maleimide compounds have been studied for years in photoinitiator-free UV curing systems [43–46]. As illustrated in Scheme 6, maleimide compound can adsorb light energy and generate small amount of free radical. In the meantime, maleimide itself is a good monomer for free radical polymerization. Compared to normal photoinitiator acrylate cases, however, its UV cure efficiency is much lower.

The new type hybrid epoxy resin adhesive is mainly composed of a liquid bismaleimide compound, partially acrylated bisphenol A epoxy resin, acrylic monomer, epoxy resin and latent curing agent. Chemical structure of typical reactive materials used is shown in Figure 4. The new type adhesive does not contain any conventional initiator, either photoinitiator or thermal initiator such as peroxide compound. It is a complete initiator free hybrid epoxy adhesive. Its UV fixture time was 5 s at 100 mW/cm² with high-pressure mercury lamp used. Good adhesion on glass substrate has been also confirmed.

FT-IR was performed to measure and analyze quantitatively cure behaviour of the adhesive sample [46–48]. The spectrum of adhesive samples cured at UV cure and UV + thermal cure conditions as well as non-cure samples was measured by the use of Varian 610-IR Fourier

![Scheme 6. Radical generation of maleimides via UV radiation.](image)
transform infrared (FT-IR) spectroscopy. **Figure 5** IR spectrum of adhesive sample cured at UV only condition was shown compared to non-cure sample. IR spectrum of adhesive samples cured at UV + thermal cure condition was shown compared to non-cure sample in **Figure 6**. The conversion rate was further calculated from the decrease of the 1405 cm\(^{-1}\) absorption peak area attributed to acrylic double bond, the 690 cm\(^{-1}\) peak area attributed to maleimide double bond and the 915 cm\(^{-1}\) peak area attributed to epoxy group. As summarized in **Table 2**, a conversion rate of 62% of acrylic and 95% of maleimide double bonds had been achieved at this UV cure condition. This result confirmed that most part of acrylic and almost all maleimide double bonds had been cured during this UV cure condition. As expected, epoxy group cured only at thermal cure condition.

Very interestingly, it was found, as shown in **Table 2**, that remained uncured acrylic double bonds at UV cure process continued to react, and the conversion rate increased eventually to 100% at post-thermal cure condition. In the meantime, conversion rate of acrylic double achieved 67 and 95% at thermal cure only condition, respectively. As described previously,
Figure 5. FT-IR spectrum of adhesive cured at UV only condition, in blue, compared to non-cure sample.

Figure 6. FT-IR spectrum of adhesive cured at UV + thermal cure condition, in blue, with compared to non-cure sample.

<table>
<thead>
<tr>
<th>Cure condition</th>
<th>C=C conversion rate (%)</th>
<th>Epoxy conversion rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV cure only, 100 mW/cm² × 30 s</td>
<td>62</td>
<td>95</td>
</tr>
<tr>
<td>UV + thermal cure, 100 mW/cm² × 30 s + 120°C × 60 min</td>
<td>100</td>
<td>96</td>
</tr>
<tr>
<td>Thermal cure only, 120°C × 60 min</td>
<td>67</td>
<td>95</td>
</tr>
</tbody>
</table>

Table 2. Conversion rate of C=C group and epoxy group measured by FT-IR.
the adhesive sample does not contain any thermal initiator component such as peroxide. Nevertheless, UV cure components of the adhesive sample showed also very good thermal curability. From epoxy resin part, conversion rate of epoxy group of adhesive sample cured at thermal cure only condition was lower than that cured at UV + thermal cure condition.

Based on this result, acrylic and maleimide double bonds reacted most probably with the epoxy curing agent, dihydrazine.

5. Summary

UV and thermal cure epoxy adhesives have been successfully used in high-end applications such as optical component bonding, sensor packaging and display panel assembly where high production efficiency and high adhesion performance are required. There are mainly two types of commercialized UV and thermal cure epoxy adhesives: UV cure cationic epoxy adhesives and hybrid UV acrylate and thermal cure epoxy adhesives. UV cure cationic epoxy adhesives are primarily composed of cycloaliphatic epoxy resin and cationic photoinitiator. UV cationic epoxy adhesives have no surface cure issue and possess low cure shrinkage and good adhesion performance but need post-thermal cure to achieve full adhesion performance. Hybrid UV acrylate and thermal cure epoxy adhesives are primarily composed of acrylate monomer, free radical photoinitiator, epoxy resin and curing agent. The hybrid epoxy adhesives combine fast UV curability of acrylate composition and high adhesion performance of thermal cure epoxy composition. A new type initiator free hybrid one-component UV and thermal cure adhesive has been also introduced. It is mainly composed of maleimide compound, acrylic monomer, partially acrylated epoxy resin, epoxy resin and latent curing agent. The new hybrid epoxy adhesive possesses good UV curability and satisfactory thermal curability and is suitable for use as high performance required applications.

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