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High performance UV and thermal cure hybrid epoxy adhesive

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Abstract. New type one component UV and thermal curable hybrid epoxy adhesive was successfully developed. The hybrid epoxy adhesive is complete initiator free composition. Neither photo-initiator nor thermal initiator is contained. The hybrid adhesive is mainly composed of special designed liquid bismaleimide, partially acrylated epoxy resin, acrylic monomer, epoxy resin and latent curing agent. Its UV light and thermal cure behavior was studied by FT-IR spectroscopy and FT-Raman spectroscopy. Adhesive samples cured at UV only, thermal only and UV + thermal cure conditions were investigated. By calculated conversion rate of double bond in both acrylic component and maleimide compound, satisfactory light curability of the hybrid epoxy adhesive was confirmed quantitatively. The investigation results also showed that its UV cure components, acrylic and bismalimide, possess good thermal curability too. The initiator free hybrid epoxy adhesive showed satisfactory UV curability, good thermal curability and high adhesion performance.

1. Introduction

Radiation curing, especially ultraviolet (UV) light curing adhesive has been widespread used in various industrial applications. It is typically one component packed room temperature stable, solvent free and can cure very fast, suitable for high speed production applications [1]. Most common UV curing adhesives are free radical curable acrylic adhesive that is mainly composed of acrylic monomer, oligomer and photo-initiator. Photo-initiator can absorb light energy to generate free radical that will immediately initiate polymerization of acrylic compositions. In this curing process, however, several small molecules are generated as byproducts. In addition, photoinitiator cannot consume completely. In the case of using benzyl dimethyl ketal (BDMK) as photoinitiator, for example, E. Sitzmann [2] described that there are at least three small molecules generated, such as benzaldehyde, methyl benzoate. These small molecular byproducts and remained photo-initiator cannot be chemically bonded to cured adhesive and thus will potentially contaminate substrates or damage adhesion performance. UV curing adhesive without photoinitiator containing will have no such problem. Maleimide compounds have been studied years for use in photoinitiator free UV curing systems [3-8]. UV light cure performance has been identified. Till today, however, there is still almost no commercial success in this approach.

Epoxy resin adhesive is one of most widely used reactive adhesives, especially for structural bonding applications where high performance is required [9]. Epoxy resin adhesive normally needs relatively long time cure that will not meet fast curing requirements for some high production efficiency applications. By combination with UV curing acrylic components, UV thermal hybrid

epoxy resin adhesive has been recently commercialized and used in actual applications such as special electronics parts assembly.

The UV thermal hybrid epoxy adhesive meets well with both high speed production and high performance requirements. For some 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 by products, remained photointiator during UV curing process on uncured adhesive compositions.

In this study, a new type one component UV thermal curable hybrid epoxy adhesive is designed. The hybrid epoxy resin adhesive is mainly composed of liquid bismaleimide compound, partially acrylated epoxy resin, acrylic monomer, epoxy resin and latent curing agent. UV cure and thermal cure behavior was investigated by FT-IR and FT-Raman spectroscopy. Glass adhesion performance was confirmed.

2. Experimental

2.1. Materials and Chemicals

Epikote 828, standard grade bisphenol A glycidyl ether epoxy resin (epoxy equivalent weight: 184 ~ 194, viscosity: 12,000 ~ 15,000 mPas/25℃), was supplied by Mitsubishi Chemical Corporation. Uvacure 1561, partially acrylated bisphenol A epoxy resin (epoxy equivalent weight: 450, viscosity: 1,000 mPas/60℃), was supplied by Daicel Allnex Ltd. Trimethylolpropane triacrylate (TMPTA) was supplied by Arkema Incorporation. Liquid bismaleimide compound was supplied by Henkel Corporation. KBM-403, 3-Glycidoxypropyltrimethoxysilane, was supplied by Shin-Etsu Chemical Co., Ltd. VDH-J (fine powder latent curing agent), 4-Isopropyl-2, 5-dioxoimidazolidine-1, 3-di(propionodihydrazide), was supplied by Ajinomoto Fine-Techno Co., Incorporation. Talc was supplied by Nippon Talc Co., Ltd. Fumed silica was supplied by Nippon Aerosil Co., Ltd. All raw materials are used directly without any further treatments. Chemical structure of main reactive materials was shown in Figure 1.

2.2. Adhesive sample preparation

The adhesive sample was composed of 28.0% Epikote 828, 22.0% Uvacure 1561, 10.0% TMPTA, 5.0% bismaleimide, 15.0% VDH-J, 1.0% KBM-403, 16.0% talc and 3.0% fumed silica. All components were added and premixed at first in a planentary centrifugal mixer. The premixed sample was further mixed on a triple roller mixer and then thoroughly degassed via full vacuum condition before use. Viscosity was measured by E-type viscometer. Pot life was determined by measuring viscosity increase during storage at 25℃ to 2 times of the initial one.

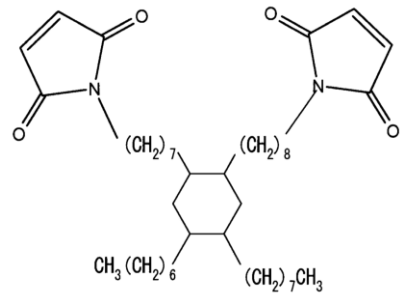
2.3. Cured sample preparation, glass transition temperature determination and adhesion strength measurement

Batch type metal halide lamp was used for UV cure. Light intensity was measured by Ushio UIT-101 UV meter. Conventional oven was used for thermal cure. Typical UV cure condition was 30 seconds at 100mW/cm^2 and thermal cure condition was 60 minutes at 120℃. UV fixture time was determined by Henkel standard method with use of slide glass as substrate. Glass transition temperature was measured by Seiko DMS 6100 dynamic mechanical analysis (DMA). Glass adhesion strength was measured according to test method ASTM D 2095. Normal slide glass was used as substrate.

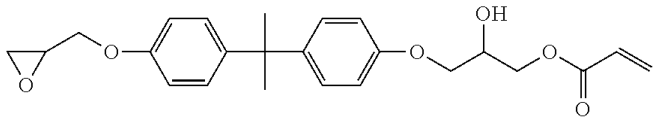
2.4. Analysis and Characterization

Varian 610-IR Fourier Transform infrared spectroscopy (FT-IR) was used to measure infrared spectrum. LabRAM HR-800 Raman Spectroscopy was used to measure FT-Raman spectrum. Conversion rate of both acrylic and maleimide double bond as well as epoxy group was calculated by peak area decrease of each specific absorption with use of absorption peak at 1505cm^{-1} attributed to aromatic ring absorption, as internal reference. The 1405cm^{-1} absorption peak was monitored for

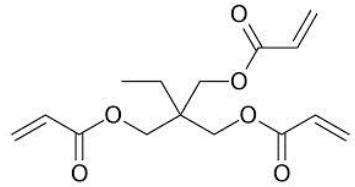
acrylic double bond [10]. The 690cm^{-1} peak area was monitored for maleimide double bond [11]while the 915cm^{-1} peak was monitored for epoxy group [12].



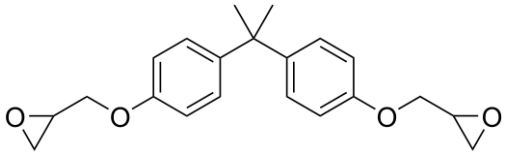
Bismaleimide compound



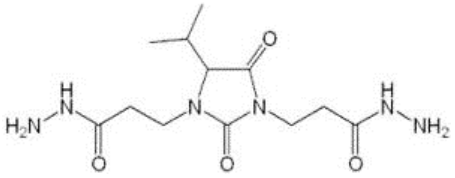
Partially acrylated bisphenol A epoxy resin



TMPTA



Bisphenol A epoxy resin



VDH-J

Figure 1. Chemical structure of key reactive materials used.

3. Results and discussion

3.1. Adhesive property and glass adhesion performance

The prepared adhesives were a high viscous milky white paste. Its viscosity measured at 25℃ was 29,6000 mPas. Pot life was 5 days at 25℃ storage. Cured sample possessed good thermal property. Glass transition temperature was 112℃.

As described previously, the adhesive sample prepared does not contain any conventional photo-initiator or thermal initiator. It is complete initiator free composition. Its UV fixture time was measured as 5 seconds at 100 mW/cm^2. This result showed that the adhesive sample possessed fast UV fixing property that can well meet high speed production requirement in various applications.

Glass adhesion strength was measured and compared at three cure conditions, i.e, UV cure only, thermal cure only and UV + thermal cure conditions. Glass adhesion strength results were summarized in Table 1. At UV cure stage, quite strong adhesion strength was obtained already. It means that this adhesive sample, even with no photoinitiator contained, showed quite good UV cure behavior. As expected, adhesion strength was much improved with post thermal cure process where epoxy part could be cured.

The sample showed very strong adhesion on glass substrate with cohesion failure. Adhesion strength at thermal cure only condition was some lower than that cured at UV and thermal cure but higher than that cured with UV only condition.

Table 1. Glass adhesion strength results.

Cure condition	Glass adhesion strength (N/mm^2)	Failure mode
UV cure only 100 mW/cm^2 x 30 sec	0.89	Interface failure
UV+ thermal cure 100 mW/cm^2 x 30 sec + 120℃ x 60 min	3.10	Cohesion failure
Thermal cure only 120℃ x 60 min	2.21	Cohesion failure

3.2. FT-IR measurements and analysis

FT-IR was performed to measure and analyse quantitatively cure behaviour of the adhesive sample. IR Spectrum of adhesive samples cured at all three conditions as well as non-cure sample was measured. Figure 2 showed and compared the measured FT-IR spectrum of adhesive sample cured with UV only condition at 100mW/cm^2 for 30 seconds, thermal cure only at 120℃ for 60 minutes and UV + thermal cure condition and that of non-cure sample. Changes of the 1405cm^{-1} absorption peak attributed to acrylic double bond, the 690cm^{-1} peak attributed to maleimide double bond and the 915cm^{-1} peak attributed to epoxy group were especially compared. As can be seen clearly that both C=C double bonds, the acrylic peak at 1405cm^{-1} and maleimide peak at 690cm^{-1}, disappeared completely after UV and thermal curing.

The conversion rate was further quantitatively calculated following the decrease of the 1405cm^{-1} absorption peak attributed to acrylic double bond, the 690cm^{-1} peak attributed to maleimide double bond and the 915cm^{-1} peak attributed to epoxy group. The calculation results were summarized in Table 2. As can be seen, conversion rate 62% of acrylic and 95% of maleimide double bonds had been achieved at this UV cure condition. This result confirmed again that major part of acrylic and almost all maleimide double bonds had been reacted during this UV cur condition. As expected, epoxy group cured only at thermal cure condition.

Very interestingly, it was found 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. At thermal cure condition without UV cure, it was also found that conversion rate of acrylic double bond and maleimide double bond achieved 67% and 95%. As described previously, the adhesive sample does not contain any thermal initiator component such as peroxide as usually used in UV thermal hybrid epoxy resin adhesive to assure complete curing of the remained acrylic composition for better performance. Nevertheless, UV cure components, i.e. acrylic and maleimide components, of the adhesive sample showed very good thermal curability. From epoxy resin part, conversion rate of epoxy group of adhesive sample cured at thermal cure only condition was some lower than that cured at UV + thermal cure condition. Based on this result, we supposed that acrylic and maleimide double bonds reacted with the epoxy curing agent. As well know, acrylic double bond can react with amines via Michael addition mechanism is shown in Scheme 1 [13-14]. Most probably, acrylic and maleimide double bond reacted with N-H in hydrazide group via Michael addition reaction.

Table 2. Conversion rate of C=C group and epoxy group measured by FT-IR.

Cure condition	C=C conversion rate (%)		Epoxy conversion rate (%)
	acrylic	bismaleimide	
UV cure only 100 mW/cm^2 x 30 sec	62	95	0
UV+ thermal cure 100 mW/cm^2 x 30 sec + 120℃ x 60 min	100	96	85
Thermal cure only 120℃ x 60 min	67	95	69

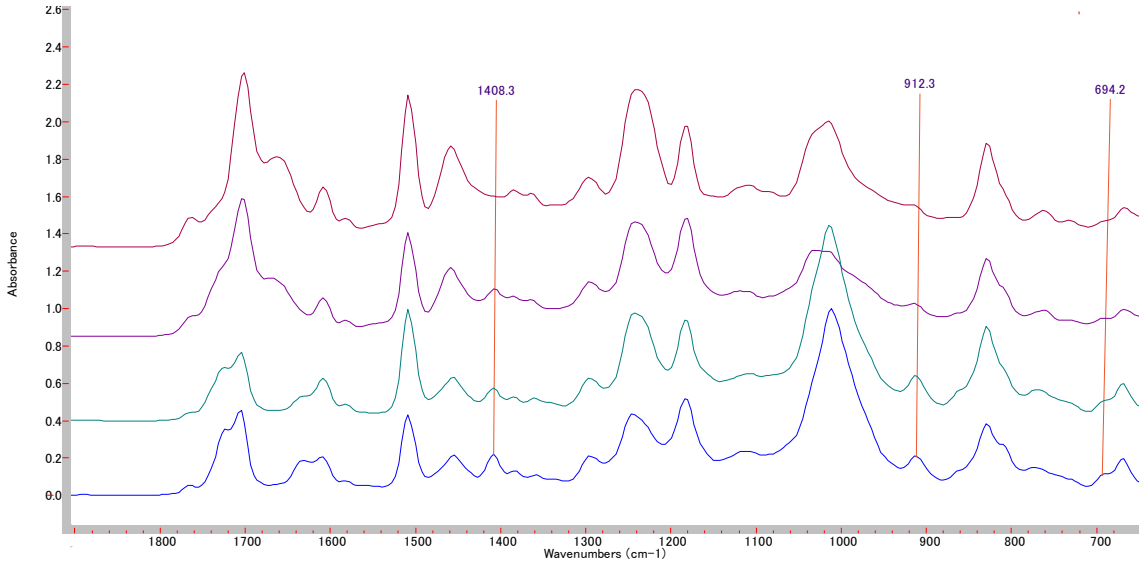


Figure 2. FT-IR spectrum of uncure sample (the bottom curve in blue colour), sample cured with UV only (the 2nd curve from bottom in light blue colour), sample cured with thermal only (the 3rd curve from bottom in purple colour) and sample cured with both UV and thermal (upper curve in red colour).

Scheme 1. Michael addition reaction between acrylic compound and amines.

3.3. FT-Raman measurements and analysis

FT-Raman analysis is a typical non-destructive analysis method with high sensitivity suitable for very trace sample measurements. The adhesive samples bonded with glass substrates cured at the same three conditions were directly used to measure FT-Raman spectrum. The conversion rate was calculated following the decrease of the 1405cm^{-1} absorption peak area attributed to acrylic double bond. Conversion rate result was summarized in Table 3. As can be seen, FT-Raman results coincided very well with FT-IR results shown in Table 2. Although there was slight difference in conversion rate values, UV and thermal cure degree trend was the same. 78% conversion rate of acrylic double bond was achieved at UV cure condition and it further increased to 97% during post thermal cure process. 88% conversion rate of acrylic double bond was obtained at thermal cure only condition. Acrylic double bond was confirmed again to possess both good UV curability and further thermal curability.

Table 3. Conversion rate of acrylic double bond measured by FT-Raman spectroscopy.

Cure condition	Acrylic C=C conversion rate (%)
UV cure only 100 mW/cm^2 x 30 sec	78
UV+ thermal cure 100 mW/cm^2 x 30 sec + 120℃ x 60 min	97
Thermal cure only 120℃ x 60 min	88

4. Conclusion

New type one component UV and thermal curable hybrid epoxy adhesive was successfully developed. The hybrid epoxy adhesive is complete initiator free composition. Neither photoinitiator nor thermal initiator is contained. The hybrid adhesive showed fast UV fixture property and very strong adhesion performance. Both FT-IR and FT-Raman results confirmed that its UV cure components possess not only good UV curability but also good thermal curability.

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