

Study on the Cure Behavior of a Novel Photocurable Material Using UPLC-Q-TOF-MS

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Abstract: An UPLC-Q-TOF-MS method is developed for cure degree measurement and cure behavior analysis on a novel photocurable adhesive material which is composed of specially designed acrylate oligomers, acrylate monomers, photo-initiators and additives such as ultra-violet absorbent, antioxidant stabilizer, optical stabilizer, etc. The photocurable adhesive material, in both cured and uncured state, were separated by Ultra-Performance Liquid Chromatography (UPLC) and the low molecular weight components were detected and determined quantitatively by high resolution Quadrupole Time-Of-Flight mass spectrometry (Q-TOF-MS) under Atmosphere Pressure Chemical Ionization (APCI) mode. Cure behaviors of all photo-reactive components in the photocurable adhesive material such as acrylate monomers and photo-initiators were studied by quantitatively measuring the amount of each reactive components in different stages of curing. Both the conversion of each acrylate monomers and photo-initiators at different curing energy conditions were calculated and discussed. Nearly full cure was obtained at cure energy of 200 mJ/cm² for 4-hydroxybutyl acrylate and acryloyl morphine, as well as the two bifunctional monomers, 1,6-hexandiol diacrylate and dimethylol tricyclodecane diacrylate. Only 42.7% and 85.0% conversion were achieved for benzyl acrylate and isobornyl acrylate, respectively while consumption of TPO, a photo-initiator, was 38.0% at this cure energy. The results showed that a minimum 2000 mJ/cm² energy condition is needed to achieve full cure of all acrylate monomers and enough decomposition of photo-initiator. This study indicated that UPLC-Q-TOF-MS is an effective and precise analytical method for cure degree measurement and cure behavior analysis on the photocurable materials.

Keywords: Photocurable, UPLC-MS, Conversion, Adhesives, Acrylate, Photo-initiator

1. Introduction

Photocurable materials have been widely used in various applications as adhesives [1-3], coatings [4-6], photoresists [7-9] and inkjet printings [10-12] because of their easily handling and fast curability. Research and development on their new applications such as 3D printing [13-14], photography [15-16], biomedical and bio-engineering [17-18] have been very actively carried out. Photocurable materials are primarily composed of photocurable oligomers, monomers, photo-initiators and additives. Cure degree measurements and cure behavior study on photocurable materials are very important for not only the determination of

suitable cure condition but also photocurable material designation as well as failure case root cause study in actual use.

Several methods such as FT-IR [19-20], UV-DSC [21], adhesion strength testing [22] have been used for cure degree measurements. All these existing methods are designed for total cure degree measurements, not suitable for cure degree determination on each individual reactive component that is very valuable for new photocurable material development. The purpose of this study is to investigate and develop a precise analytical method that can be used for cure degree determination on individual reactive components for photocurable materials.

Ultra-Performance Liquid Chromatography – Mass

Spectrometry (UPLC-MS) is a relatively new analytical technique that combines superior chromatographic separation with the high-performance mass spectrometric detection [23-26]. Recently, UPLC-MS has been applied successfully to detect four acrylate monomers in the recycled Polyethylene Terephthalate (rPET) materials using Electrospray Ionization (ESI) and Triple Quadrupole (QqQ) mass analyzer [27].

In this study, an UPLC-MS method is developed for cure behavior study on a novel photocurable adhesive material. This photocurable material is our recent commercialized liquid optical clear adhesive designed for use in touch panel assembly [28-29]. It is composed of specially designed acrylate oligomers, acrylate monomers, photo-initiators and additives such as ultra-violet absorbent, antioxidant stabilizer, optical stabilizer, etc. The photocurable material, in both cured and uncured states, were separated by ultra-performance liquid chromatography and the low molecular weight components were detected and determined quantitatively by Quadrupole Time-Of-Flight (Q-TOF) mass spectrometry under Atmosphere Pressure Chemical Ionization (APCI). Q-TOF mass analyzer provides high-resolution and high accuracy mass detective ability for confident identification and quantification. This method is effective to determine the cure behaviors of acrylate monomers and photo-initiators in this novel photocurable adhesive material.

2. Materials and Methods

2.1. Materials and Reagents

Production batch novel photocurable adhesive sample was used directly without any treatment. Their cured samples were prepared by curing the adhesive material via NPF polarizer adhered glass at five different curing energy conditions, i.e., 200, 500, 1000, 2000 and 3000 mJ/cm². NPF (Nitto Polarizing Film) was supplied by Nitto Denko Corporation (Osaka, Japan). UV equipment was ECS-4012XS convey type supplied by Eye Graphics Co., Ltd. (Tokyo, Japan). UV lamp was M04-L41 metal halide lamp supplied also by Eye Graphics Co., Ltd. (Tokyo, Japan). UV energy was detected by UIT 250 UV meter supplied by Ushio Incorporation (Tokyo, Japan). Same grade acrylate monomers, photo-initiators and additives as those contained in the novel photocurable adhesive were used in analysis without any treatment. All analytical reagents, i.e. solvents acetonitrile, water, tetrahydrofuran, were UPLC-MS grade or above from Thermal Fisher Scientific (Waltham, MA, USA). Ammonium acetate and Leucine encephalin were chromatographic or spectroscopic grade from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Preparation of Standard Solutions

50 mg each reference standard of acrylate monomer, photo-initiator or other additives was accurately weighed into a 10 mL volumetric flask to prepare reference standard stock solutions in acetonitrile. A series of dilution was carried out to prepare the calibration solutions at different concentrations.

The stock and calibration solutions were sealed and kept at -18°C free of light for up to three months.

2.3. Preparation of Analytical Samples

20 mg cured or uncured photocurable adhesive materials were accurately weighed and 1 mL solvent mixture of acetonitrile and tetrahydrofuran (volume ratio: 4:1) was added. The samples were completely dissolved with ultrasonic treatment at room temperature for 1 hour and filtered through a 0.22 µm PVDF syringe filter (Thermal Fisher Scientific) before analysis.

2.4. UPLC - Mass Spectrometry Measurement

The reference standard and adhesive material solutions were analyzed by using ACQUITY H-class UPLC with Xevo G2-XS Q-TOF mass spectrometry manufactured by Waters Corporation (Milford, MA, USA). Mobile phase A is 10 mM Ammonium Acetate and B is Acetonitrile. HSS T3 1.8 µm 2.1*100mm column with a guard column (column temperature was kept at 40°C). Flow rate: 0.4 mL/min. The gradient started with 30% of A and increased to 100% B in 5 min and kept until 12 min, then resumed to starting condition. Total run time is 15 min. Mass spectrometry was acquired under positive ion APCI mode with a lock spray of Leucine Enkephalin. APCI probe temperature 550°C. TOF was operated under high resolution MS^E centroid mode with scan time 0.5 sec and corona current 3.0 µA. Source Temperature: 120°C; Cone Gas Flow: 30.0 L/H; Desolvation Gas Flow: 500.0 L/H; Scan Mass: 50.0 ~ 1200 Da.

3. Results

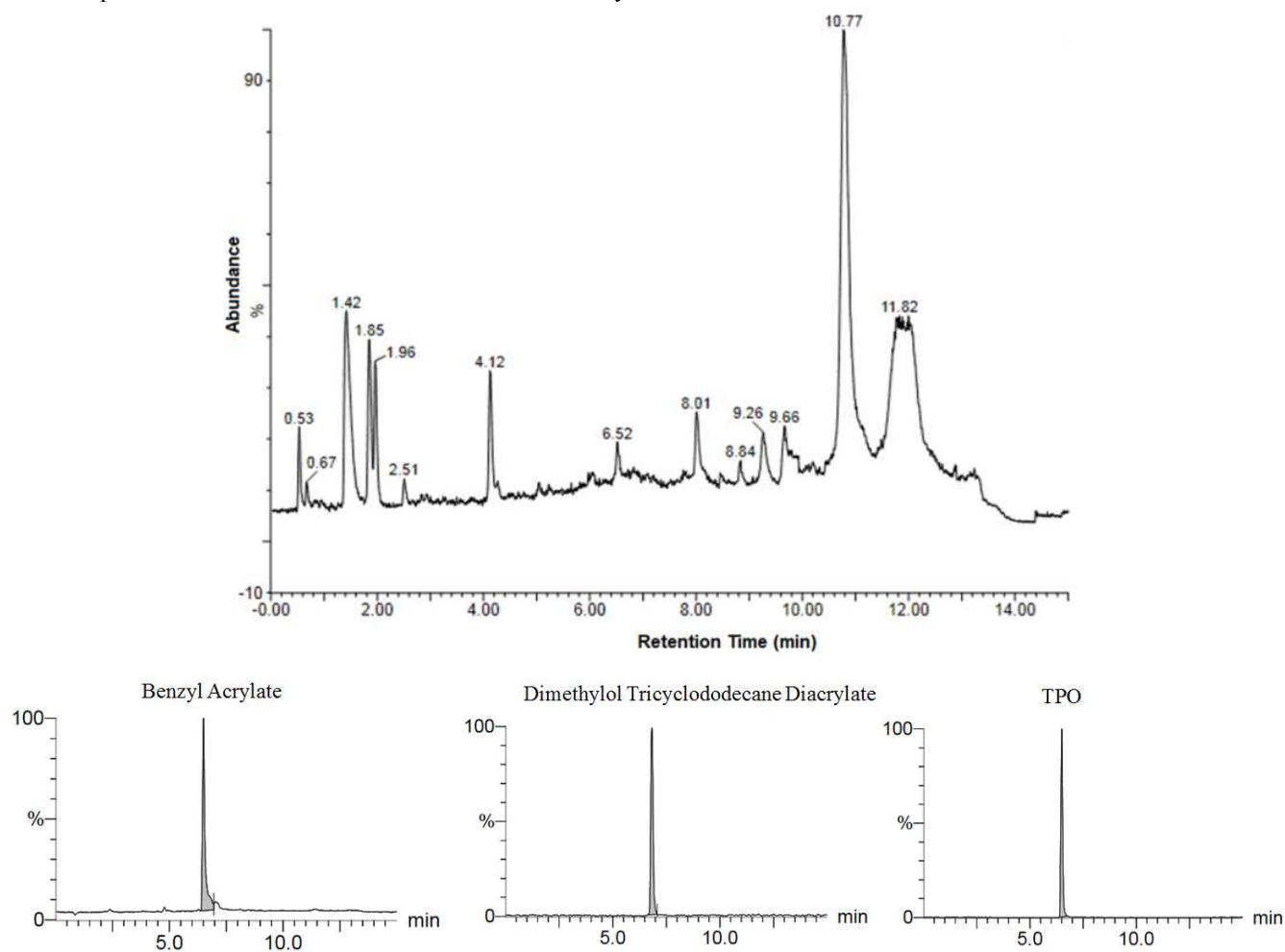
3.1. Separation, Detection and Quantitative Analysis

The photocurable adhesive material was separated by reverse phase UPLC under a gradient program in an aqueous and solvent system as described above. Each component is detected and determined by high resolution Q-ToF mass spectrometer under positive ion APCI ionization scan mode. Figure 1 shows the typical Total Ion Chromatogram (TIC) of a uncured photocurable adhesive material. Ultra-performance liquid chromatography (UPLC) provided excellent separation of multiple components in the product. The characteristic mass spectrometric peak for each targeted analyte was determined using reference standard as either the molecular ion or the most abundant fragment ion. These ions were extracted from the total ion chromatogram (TIC) to pull out the Extracted Ion Chromatogram (EIC) of each compound for further quantification, as shown in Figure 1 for benzyl acrylate, dimethylol tricyclodecane diacrylate and TPO as example. The high resolution and high accuracy Q-TOF-mass spectrometry enabled confident peak extraction and confirmation for each analyte free of interference from the background and sample matrix.

Using this approach, the acrylate monomers, photoinitiators and additive components formulated in the product have been separated and detected successfully. These compounds

included three mono-functional acrylate monomers, i.e. isobornyl acrylate, 4-hydroxybutyl acrylate and 4-acryloylmorphine, as well as two bifunctional acrylate monomers, i.e. 1, 6-hexanediol diacrylate and dimethylol tricyclodecane diacrylate. An additional acrylate monomer, benzyl acrylate, which was not formulated intentionally, was also detected. It was contained in the acrylate oligomers used in this photocurable adhesive material for viscosity

adjustment purpose. Two photoinitiators, 1-hydroxy-cyclohexyl-phenyl-ketone and diphenyl-(2,4,6-trimethylbenzoyl)-phosphine oxide (abbreviated as TPO), were also detected. Other additives such as UV absorbers, thermal stabilizer, optical stabilizers formulated for reliability performance withstanding have all been detected and determined successfully.



Top: Total Ion Chromatogram (TIC); Bottom: Extracted Ion Chromatograms (EIC) of Benzyl Acrylate, Dimethylol Tricyclodecane Diacrylate and TPO

Figure 1. UPLC-MS Chromatograms of the Uncured Photocurable Adhesive.

3.2. Calibration and Quantitative Analysis

Standard stock solutions of all detected components with 100 ppm concentration in acetonitrile were prepared and further diluted to 7 additional different concentration levels from 1 to 80 ppm as shown in Table 1 as calibration solutions. Extracted ion chromatograms (EIC) were used for peak integration and the peak areas were measured for calculation of the amount of each analyte by using external standard calibration method. All compounds showed good linear calibration within the wide dynamic range with R^2 greater than 0.99. Figures 2 and 3 show the calibration curves for benzyl acrylate, the monofunctional monomer, dimethylol tricyclodecane diacrylate, the bifunctional monomer, respectively. Further validation indicated that the repeatability

among 5 replicates was typically within 5% RSD except for benzyl acrylate which is <10% RSD. Spike recovery for all compounds were between 88~100% with a LOQ of 1 ppm.

Table 1. Calibration Solution Preparation.

NO.	Concentration (ppm)	Standard monomer solution (μ L)	Solvent (μ L)
1	1	10	990
2	2	20	980
3	5	50	950
4	10	100	900
5	20	200	800
6	50	500	500
7	80	800	200
8	100	1000	0

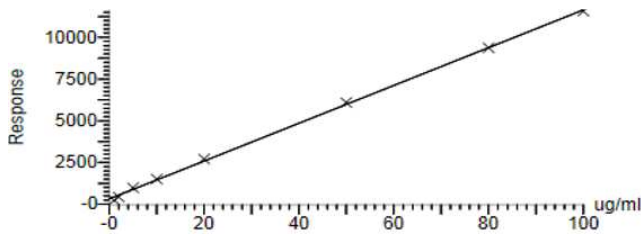


Figure 2. Calibration Curve of Benzyl Acrylate.

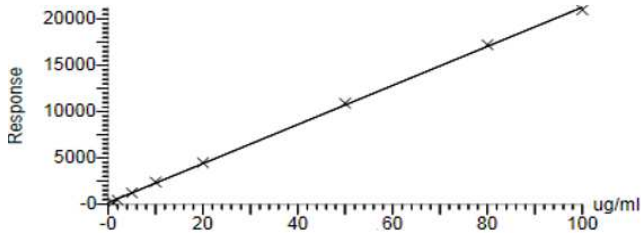


Figure 3. Calibration Curve of Dimethylol Tricyclodecane Diacrylate.

3.3. Cure Behavior Measurements on Acrylate Monomers

By quantitatively measuring the amount of each acrylate monomer in the cured photocurable adhesive samples prepared using five different cure energies and comparing with that of uncured material, conversion of all acrylate monomers including four monofunctional and two difunctional ones can be calculated. The calculation scheme of conversion is shown in Equation 1. Figure 4 shows the analytical result of conversion of isobornyl acrylate, which reached 85.0% at cure energy of 200 mJ/cm². It increased steadily to 98.6% when cure energy was continuously applied for up to 2000 mJ/cm² and finally reached 100% at 3000 mJ/cm².

$$= \left(1 - \frac{\text{Amount of target compound in the cured adhesive}}{\text{Amount of target compound in the uncured adhesive}}\right) \times 100\%$$

Equation 1. Calculation Formula on Conversion.

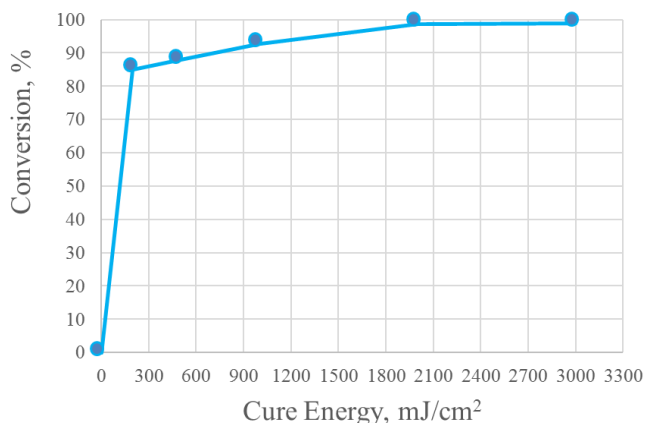


Figure 4. Conversion of Isobornyl Acrylate.

Conversion result of 4-hydroxybutyl acrylate is shown in Figure 5. This acrylate monomer cured much faster and reached 100% already at only 200 mJ/cm² cure energy applied.

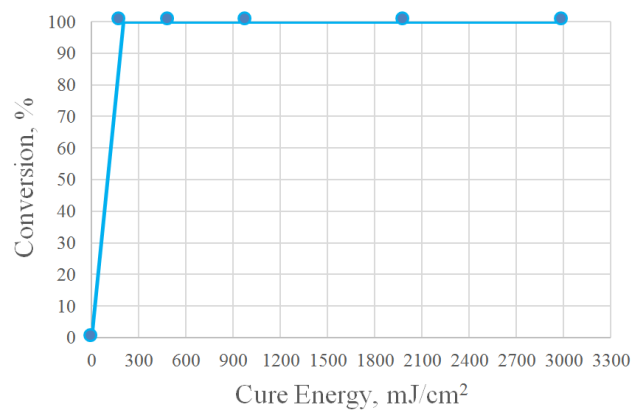


Figure 5. Conversion of 4-Hydroxybutyl Acrylate.

Conversion result of benzyl acrylate is shown in Figure 6. Benzyl acrylate cured relatively slowly. Its conversion was 42.7% at cure energy of 200 mJ/cm². It increased steadily to 93.9% when cure energy was continuously applied for up to 2000 mJ/cm² and reached 95.6% at 3000 mJ/cm² radiation condition.

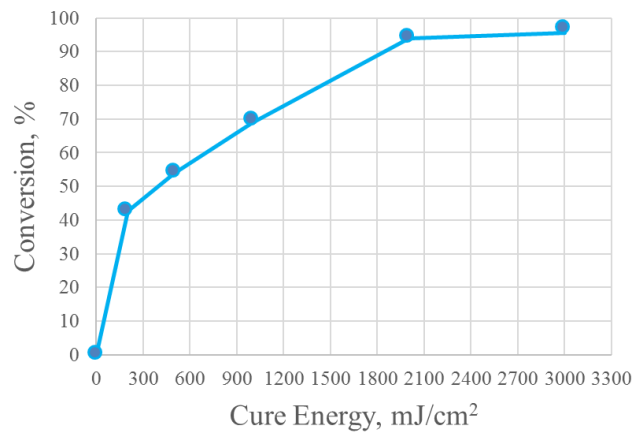


Figure 6. Conversion of Benzyl Acrylate.

Conversion result of acryloyl morphine is shown in Figure 7. Acryloyl morphine cured very fast. Its conversion reached 95.8% at cure energy of 200 mJ/cm². It increased continuously to 98.6% when cure energy was continuously applied for up to 2000 mJ/cm² and remained unchanged at 3000 mJ/cm² radiation condition.

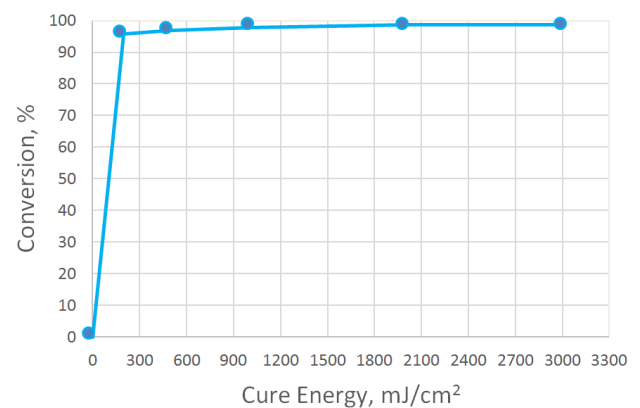


Figure 7. Conversion of Acryloyl Morphine.

Figure 8 and Figure 9 show the conversion result of the two bifunctional monomers, 1, 6-hexanediol diacrylate and dimethylol tricyclodecane diacrylate, respectively. Both monomers cured very fast. Conversion of 1, 6-hexanediol diacrylate reached 98.7% at cure energy of 200 mJ/cm² and increased slightly to more than 99% when cure energy was continuously applied. Conversion of dimethylol tricyclodecane diacrylate was 98.1% at cure energy of 200 mJ/cm². Its conversion increased to around 99% when cure energy was continuously applied.

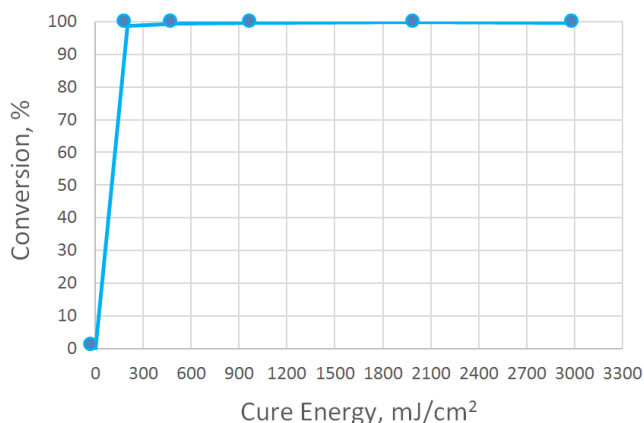


Figure 8. Conversion of 1,6- Hexanediol Diacrylate.

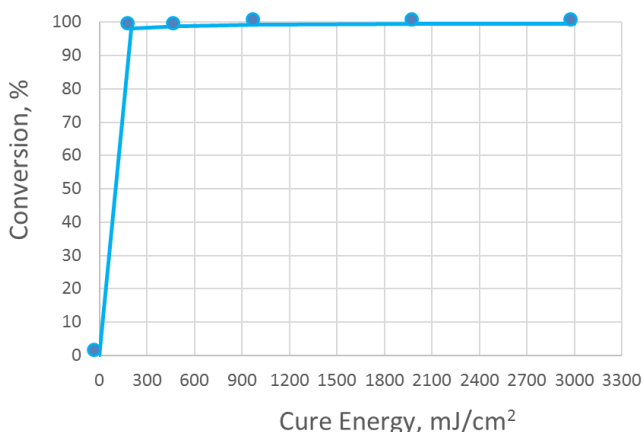


Figure 9. Conversion of Dimethylol Tricyclodecane Diacrylate.

3.4. Decomposition Measurements on Photoinitiator and Additive

By quantitatively measuring the amount of each photoinitiator and additive in above five cured photocurable adhesive materials and comparing with that of uncured material, their conversion can be calculated. The results showed that only TPO, the visible light curable type photoinitiator, had changed at the testing condition. Figure 10 shows the analytical result of conversion of TPO, which was 38.0% at cure energy of 200 mJ/cm². It increased steadily to 92.5% when cure energy was continuously applied for up to 2000 mJ/cm² and increased slightly to 95.3% at 3000 mJ/cm². There is no change detected for normal photoinitiator. This is because normal low wavelength UV light was filtered out by the NPF glass and only relatively long wavelength visible light

could pass through the adhesive material during this curing condition.

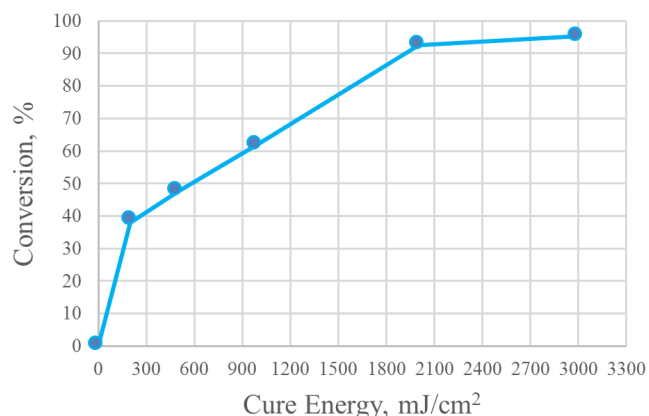


Figure 10. Conversion of TPO.

4. Discussion

The above analytical results showed that a minimum 2000 mJ/cm² cure energy is needed to achieve over 90% conversion for all acrylate monomers. Cure speed differs greatly among these acrylate monomers, as compared in Figure 11. Nearly full cure was obtained at cure energy of only 200 mJ/cm² for 4-hydroxybutyl acrylate and acryloyl morphine, as well as the two bifunctional monomers, 1, 6-hexanediol diacrylate and dimethylol tricyclodecane diacrylate while only 42.7% and 85% conversion rates were achieved for benzyl acrylate and isobornyl acrylate at this cure energy. Sufficient energy application is also required to assure enough photoinitiator consumption because the residue of photoinitiator is believed to damage reliability performance during actual use. The results indicated that a minimum 2000 mJ/cm² cure energy is needed to achieve over 90% decomposition of the photo-initiator, TPO.

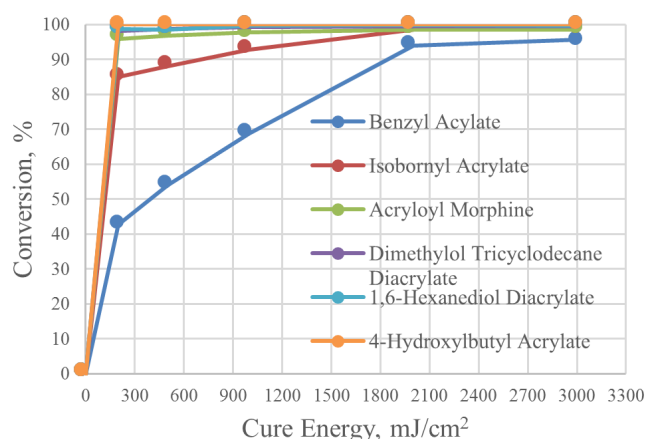


Figure 11. Comparison Conversion of Acrylate Monomers.

5. Conclusion

UPLC-Q-TOF-MS can be used to effectively detect and quantify the low molecular weight components such as acrylate monomers, photo-initiators and additives in the

photocurable materials. By quantitatively measuring the amount of each photo-reactive components such as acrylate monomers and photo-initiators in the cured photocurable adhesive materials and comparing with that of uncured material, their conversion, cure behavior and suitable cure condition can be reliably determined. Cure behavior results of each reactive components can be also used for new photocurable material development by selection of suitable components. This study demonstrates that UPLC-Q-TOF-MS is a very useful analytical tool for cure degree measurement and cure behavior study for photocurable materials.

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