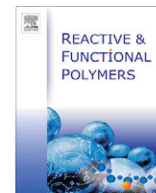
Reactive & Functional Polymers 73 (2013) 641–646

Contents lists available at SciVerse ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react



Preparation and characterization of dual curable adhesives containing epoxy and acrylate functionalities

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ARTICLE INFO

Article history:
Received 11 November 2012
Received in revised form 21 January 2013
Accepted 22 January 2013
Available online 29 January 2013

Keywords:
Epoxy
Acrylate
Carboxyl
Dual curing
Crosslinking
Adhesive

ABSTRACT

Bisphenol A type methacrylate, glycidyl methacrylate, acrylic acid and a trifunctional monomer were cured using both ultraviolet (UV) and thermal methods. The UV and thermal curing behavior of these components was evaluated using photo-differential scanning calorimetry (Photo-DSC) and Fourier Transform infrared spectroscopy (FT-IR) analyses, as well as gel fraction and pendulum hardness measurements. The reaction rate was fast, and an increasing amount of C=C double bond character was observed by FT-IR, demonstrating an effective reaction in the presence of both UV irradiation and heat. The gel fraction analysis also confirmed the formation of crosslinks in the structure after the curing process. The pendulum hardness test revealed the nature of the curing process at different UV doses after UV and thermal curing. The adhesion strength was also evaluated as a function of epoxy group concentration, demonstrating that adhesion increased with increasing epoxy group content. The thermal degradation characteristics were monitored by thermal gravimetric analysis (TGA). The bonding between the epoxy and carboxyl groups resulted in a delayed degradation of the cured adhesive.

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1. Introduction

UV curing technology has been used because of its many advantages, including fast reaction rates, solvent-free curing at room temperature, low energy consumption, and low capital investment [1]. The applications of this technology include electronic, printing, optical and electro-optical materials, as well as the use as adhesives, sealants, coatings and surface modification components [1–3]. Recently, the application of UV-curing technology has been extended to the assembly of various electronic devices for the purpose of encapsulation, adhesion, and protection [4–7]. However, the UV reaction does not take place in the shadow area, so another method is necessary for curing the uncured area. Thus, a dual curing technology, typically UV and thermal curing, has been developed to address this problem [8–12].

Epoxy (meth)acrylates contain an epoxy backbone and an unsaturated (meth)acrylate functionality in their end groups. Accordingly, the curing process is rapid, and three-dimensional molecular structures can be formed by UV irradiation. Epoxy (meth)acrylates based on diglycidyl ether bisphenol are commonly used because they allow for facile tuning of the adhesion, hardness and chemical resistance properties [13]. Their applications include electronics, construction and aerospace industries because of their good fluidity, physical strength and cost advantage [14–16]. In particular, the excellent adhesion, durability, heat, solvent and chemical resistance of diglycidyl ether bisphenol make it a popular adhesive for electronic devices [17–19].

Decker et al. [20] monitored the UV curing behavior of a diacrylate bisphenoxy-A derivative with a bicycloaliphatic diepoxide moiety using infrared spectroscopy. Chen et al. [21] observed the dual curing kinetics and morphology of an epoxy with a dimethacrylate moiety. The mechanical properties of epoxy adhesives modified with acrylate liquid rubber were investigated by Ratna and Banthia [22]. Bajpai et al. [23] studied a solvent-free UV-curable epoxy resin. Nowers and Narasimhan [24] examined the complex reaction kinetics during the formation of an epoxy-acrylate interpenetrating polymer network (IPN). Chattopadhyay et al. [25] explored the correlations between structure and properties using different types of epoxy resin as a function of (meth)acrylate crosslinker concentration. Chiang and Hsieh [26] studied UV-curable epoxide resins with tertiary amines as thermal accelerators.

In this study, the bisphenol A-type ethoxylated dimethacrylate was used as the base material and treated with different amounts of epoxy groups, which react with the carboxyl groups of acrylic acid in the presence of heat. A trifunctional acrylate monomer was incorporated as the crosslinker. All components contain C=C double bonds so they can react with one another and form a crosslinked structure in the presence of UV irradiation. The resulting materials function as adhesives upon the completion of the dual curing process. The curing behavior was monitored by Fourier

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1381-5148/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.reactfunctpolym.2013.01.012

Transform infrared spectroscopy, photo-differential scanning calorimetry, pendulum hardness and gel fraction analyses. The adhesion strength was also measured using a universal testing machine after the dual curing and aging processes. The thermal degradation behavior under heating and isothermal conditions was evaluated by thermogravimetric analysis.

2. Experimental

2.1. Materials

Bisphenol A (ethoxylated)$_{10}$ dimethacrylate (BPADMA, Miwon Specialty Chemical Co. Ltd., Republic of Korea) was used to incorporate the benzene ring into the polymer backbone. Glycidyl methacrylate (GMA, Junsei Chemicals, Japan) was used to introduce the epoxy ring for reaction with the carboxyl group of acrylic acid (AA, Samchun Chemicals, Republic of Korea). Trimethylolpropane triacrylate (TMPTA, Miwon Specialty Chemical Co. Ltd., Republic of Korea) was the multifunctional crosslinker in this system. The photoinitiator was 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173, BASF, Germany), whereas the catalyst for the reaction between epoxy and the carboxyl group was triethylamine. All reagents were used without any further purification.

2.2. Preparation of dual curable adhesive

Table 1 provides the blend ratios for the samples prepared in this study. The ratio of the epoxy and carboxyl groups to BPADMA was varied, while equal amounts of the epoxy and carboxyl groups were maintained. BPADMA, GMA, AA, TMPTA, the photoinitiator and the catalyst were blended at room temperature using a paste mixer (Daewha Tech, Republic of Korea) for 5 min at 1500 rpm. The heat generated during the blending process was not considered in this study.

2.3. Curing behavior

2.3.1. Photo-differential scanning calorimetry (Photo-DSC)

The UV curing behavior was observed at 25 °C using a photo-DSC (Q-200, TA Instrument, USA) equipped with a photocalorimetric accessory that uses UV/visible light. The sample (average weight of 7 mg) was loaded into an open aluminum DSC pan with a diameter of 5 mm. The UV/visible light wavelength of 250–650 nm from a 200 W high pressure mercury source was transmitted into the sample chamber with an intensity of 14 mW/cm^2. Approximately 2 min after loading the sample, the UV irradiation was performed for 5 min at 25 °C.

2.3.2. Fourier-transform infrared (FT-IR) spectroscopy

The IR spectra were obtained before and after the UV and thermal curing processes using an FT-IR 6100 instrument (JASCO, Japan) equipped with an attenuated total reflectance (ATR) accessory. A 40-μm-thick film prepared by thermally curing for 1 h at 150 °C and then UV curing with a UV dose of 1500 mJ/cm^2 was used in these experiments. The transmission range of the ATR crystal was 4000–650 cm^{-1} with a resolution of 4 cm^{-1}. The curing behavior of a dual-curable adhesive was monitored by evaluating the change in the peak positions of the epoxy group at 910 cm^{-1} and of the C=C double bond at 810 cm^{-1}. The peaks associated with these groups decreased or disappeared as the reaction between the epoxy and the carboxyl group and the crosslinking between the C=C double bonds took place.

Table 1
Blend ratios of dual curable adhesives.

Bisphenol A dimethacrylate (mol)	2	2	2	2	2
Glycidyl methacrylate (mol)	0	0.2	0.5	1	1.5
Acrylic acid (mol)	0	0.2	0.5	1	1.5
Photoinitiator (phr)	1	1	1	1	1
Triethylamine (phr)	2.5	2.5	2.5	2.5	2.5
Trimethylolpropane triacrylate (phr)	15	15	15	15	15

2.3.3. Gel fraction

The gel fraction was measured to confirm the crosslinked molecular structure of the adhesive after UV and thermal curing. In this study, a UV cured film prepared using an irradiation of 1500 mJ/cm^2 and a dual-cured film prepared by UV curing with a dose of 1500 mJ/cm^2 and then thermal curing for 1 h at 150 °C were used. Films of 0.2 g were soaked in toluene at 50 °C for 24 h. The soluble part was removed by filtering and the remaining insoluble part was dried at 50 °C until a constant weight was obtained. The gel fraction was calculated using the following equation:

$$\text{Gel fraction } (\%) = (W_1/W_0) \times 100$$

where W_0 is the initial weight of the sample, and W_1 is the solvent-extracted weight [27].

2.3.4. Pendulum hardness

A pendulum hardness tester (Ref. 707PK, Sheen Instruments Ltd., United Kingdom) was used to monitor the surface hardness as a function of curing degree during the UV, thermal and dual-curing processes by employing the König method. Each specimen was prepared by coating samples on a glass substrate with a thickness of 40 μm and then either UV curing using 1500 mJ/cm^2, thermally curing for 1 h at 150 °C, or dual curing by UV irradiation followed by heating for 1 h at 150 °C. The surface hardness of the UV, thermal or dual-cured films with different UV doses and reaction times was measured after curing. The pendulum oscillation time was from 6° to 3° at 25 °C and 50 ± 2% R.H. The pendulum hardness test is based on the principle that the amplitude time of the pendulum oscillation increases with increasing hardness of the measured surface (ASTM D4366). The König pendulum consists of a triangular open framework with an adjustable counterpoise weight of 200 ± 0.2 g. The pendulum pivots on two bearings, which are 5 mm in diameter and rest on the test surface [28].

2.4. Adhesion strength

The adhesion strength was measured at ambient temperature by a pull-off method using a universal test machine (UTM, Zwick. Co., Germany). For evaluating the adhesion strength, specimens were prepared by overlapping two glass substrates with dimensions of 50 × 100 × 5 (mm^3) crosswise and then placing an adhesive between them with a thickness of 20 μm and an area of 50 × 50 (mm^2). Subsequently, the specimens were cured at 1500 mJ/cm^2 and 150 °C for 1 h. The adhesion strength measurement was performed at room temperature with a crosshead speed of 2 mm/min. The specimens were aged at 250 °C for 2 h and then tested under the same conditions to determine whether the strength was maintained after aging.

2.5. Thermal gravimetric analysis (TGA)

The thermal degradation behavior was observed using a thermal gravimetric analysis (TGA 4000, PerkinElmer, USA). A 5–10 mg sample of dual-cured films obtained by irradiating at 1500 mJ/cm^2 and heating at 150 °C for 1 h were loaded into the sample tray. The temperature was increased from 25 to 600 °C at a rate of 10 °C/min under a nitrogen atmosphere. The degradation

in the isothermal state was also observed by measuring the weight loss over 1 h at 250 °C under a nitrogen atmosphere.

3. Results and discussion

3.1. Fourier-transform infrared (FT-IR) spectroscopy

In Fig. 1, a peak at approximately 810 cm^{-1} was observed, which is related to the C=C double bond stretching peak [29]. After UV curing, the C=C double bond peak at 810 cm^{-1} decreased significantly as the double bonds reacted with one another. The reaction was nearly complete in the presence of UV irradiation, as indicated by the fact that the peak at 810 cm^{-1} exhibited almost no difference after the UV curing and thermal curing processes. The epoxy group peak at approximately 910 cm^{-1} [30,31] exhibited a shoulder and disappeared after the thermal curing process, meaning that the epoxy group reacted with the carboxyl groups and produced the hydroxyl group [32,33]. Indeed, a hydroxyl group peak at approximately 3500 cm^{-1} was observed in the spectra. The proposed schematic diagram of UV and thermal curing processes is shown in Fig. 2.

3.2. Photo-differential scanning calorimetry (Photo-DSC)

The UV-curing behavior can be monitored by photo-DSC in the presence of UV irradiation. The heat of the reaction can be determined by measuring the heat flow during the UV irradiation. Thus, the relative reactivity or reaction rate also can be evaluated from these data. Fig. 3 shows the heat flow of each sample over the course of the reaction. In this plot, the UV irradiation was initiated 2 min after loading the sample, and the reaction between the C=C double bonds occurred immediately in the presence of UV light. A sharp heat flow peak related to the reaction kinetics is observed in the thermogram. An increase in the AA and GMA concentrations resulted in an increase in the C=C double bond character because these molecules contain C=C double bonds in their (meth)acrylate groups. Thus, the heat flow increased due to an increase in the relative abundance of reactive C=C double bonds, resulting in a very fast reaction rate. After 3 min, the reaction was nearly complete which was apparent because the heat flow decreased to zero.

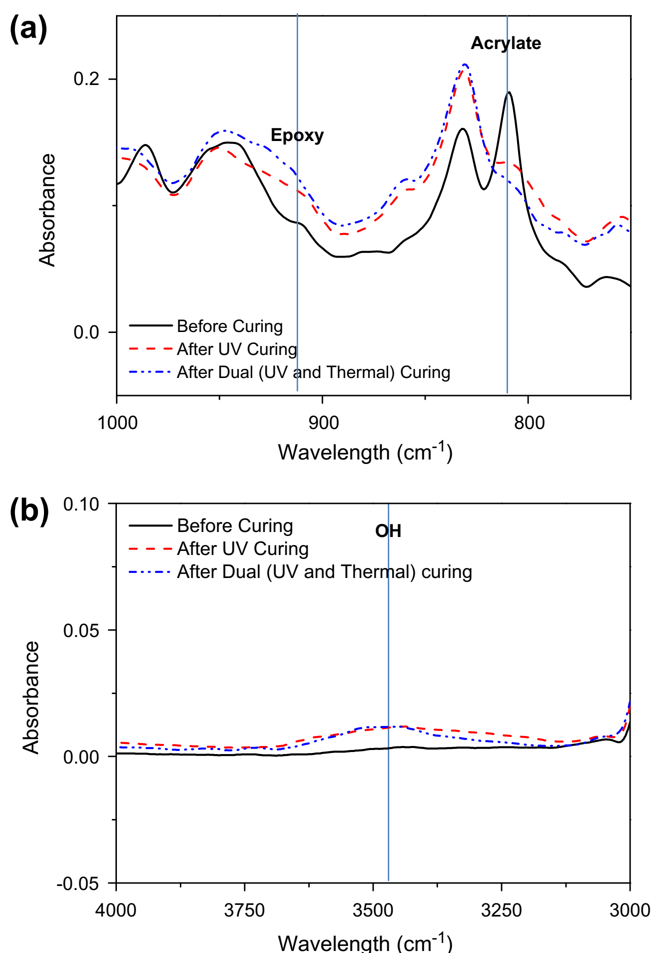

Fig. 1. FT-IR spectra of a dual cured adhesive prepared using 1 mol of AA and GMA before and after the UV and thermal curing process.

3.3. Gel fraction

As shown in Fig. 4, a gel fraction corresponding to a crosslinking degree of 96–97% was achieved with the use of UV curing (in the absence of thermal curing). No significant changes were observed with respect to the epoxy group concentration because the C=C double bonds in the(meth)acrylate groups of BPADMA, AA, GMA and TMPTA immediately reacted with one another in the presence of UV irradiation and formed an insoluble crosslinked structure [27,34–36]. Whereas the amount of epoxy group did not significantly affect to the formation of the crosslinked structure, the amount of the multifunctional component (TMPTA in this case) had an effect on the degree of crosslinking [37]. The gel fraction increased slightly to 98% after the thermal curing process. This effect is due to the bonding between the epoxy and carboxyl groups [32], but its influence was not as significant as that of the bonding between the C=C double bonds that originates from the (meth)acrylate, resulting in a minimal increase in the gel fraction.

3.4. Pendulum hardness

Fig. 5a illustrates the change in surface hardness as a function of UV dose and epoxy group concentration in the presence of only UV curing. The surface hardness is associated with the degree of curing achieved by varying the UV dose [38]. That is, the surface hardness increased with an increasing UV dose due to the enhanced reaction between the C=C double bonds, resulting in a tack-free film. A UV dose of 300–1200 mJ/cm^2 was not enough, whereas a dose of 1500 mJ/cm^2 was sufficient for the complete curing of the adhesive. After thermal curing, the surface hardness exhibited an increase due to the bonding between the epoxy and carboxyl functional groups relative to the sample cured only by UV, as shown in Fig. 5b.

The thermal curing behavior is plotted in Fig. 5c as a function of time. A tack-free film was not achieved by only thermal curing for 60 min, meaning incomplete curing took place. In case of thermally-cured film for 5 min, the film remained uncured although the surface hardness was high. The substrate property was observed instead of the property of the adhesive film. The surface hardness decreased significantly after 30 min because the sticky surface caused by the crosslinked structure to react with each component, especially the epoxy and carboxyl groups. Upon further exposure to heat, a more crosslinked structure was obtained due to the additional reaction process, resulting in a stickier surface. However, the crosslinking density due to thermal curing alone was too low to form a tack-free surface. Although there are enough epoxy and carboxyl groups, the reaction is incomplete at 150 °C, leading to a very low degree of curing. Thus, the surface hardness is nearly the same regardless of the amount of AA and GMA. The molecular motion was restricted as the crosslinking took place, limiting the ability carboxyl and epoxy to react with one another. As a result, only a minor difference in the surface hardness is

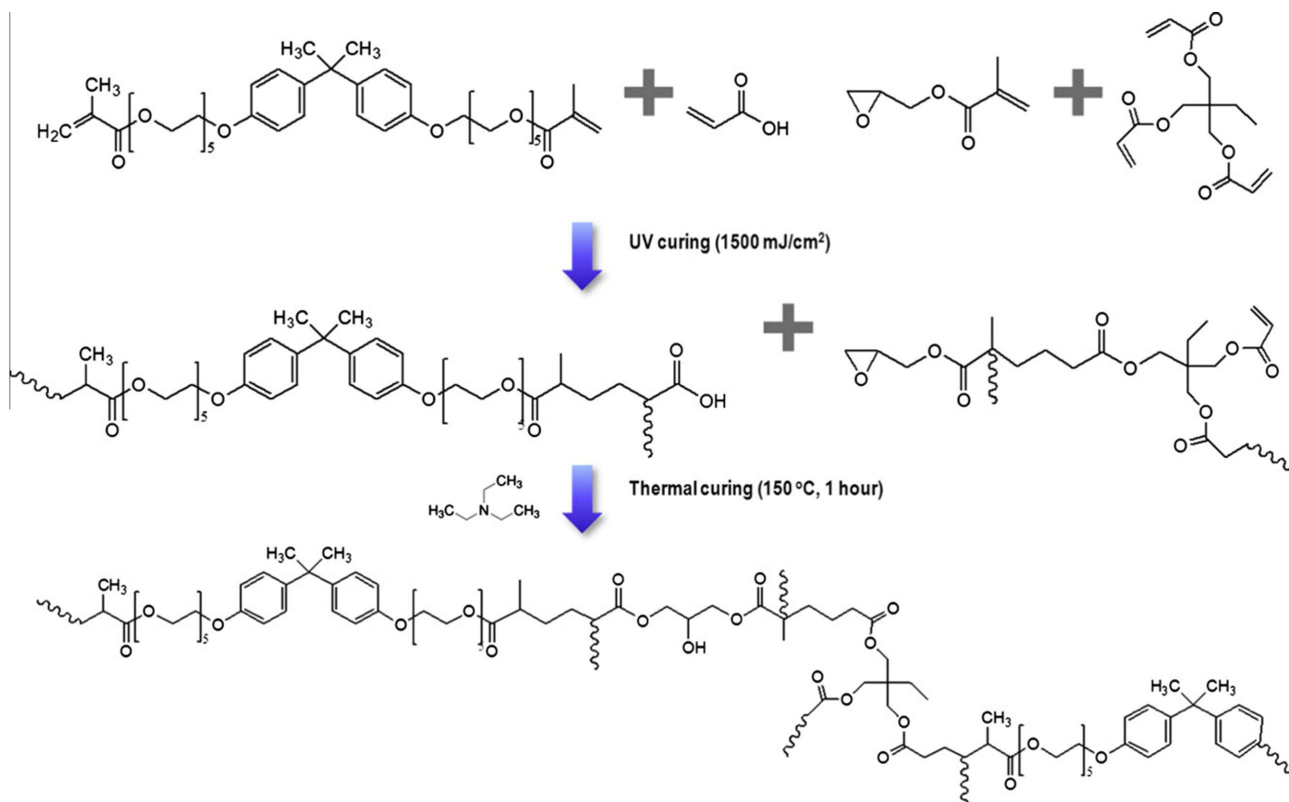

Fig. 2. Schematic diagram of the reaction during the UV and thermal curing process.

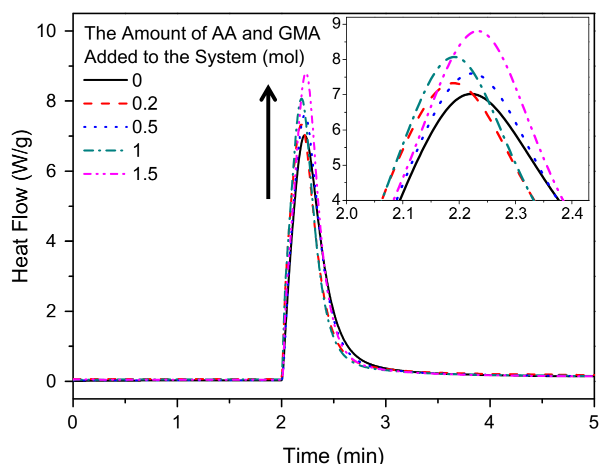

Fig. 3. Photo-DSC thermograms of adhesives after UV curing.

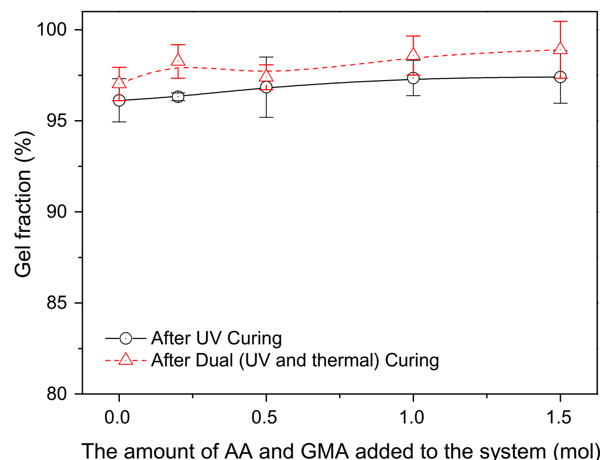

Fig. 4. The gel fraction of samples after curing.

observed despite variations in the amount of epoxy and carboxyl functionalities.

In Fig. 5d, the surface hardness after dual curing is provided as a function of epoxy and carboxyl group concentration. The surface hardness initially decreased due to the incorporation of epoxy and carboxyl groups but subsequently increased with increasing epoxy and carboxyl group concentrations. In this study, GMA and AA were used to introduce the epoxy and carboxyl groups. These molecules have smaller structures than that of BPADMA. Therefore, the polymer chain structure formed after curing remained small because these small molecules limited the ability to form long polymer chains in comparison to the structure formed in the absence of these molecules. In turn, this effect resulted in a lower surface hardness [39,40]. When the amounts of epoxy and carboxyl groups were 0.2 and 0.5 mol, the bonding between the epoxy and the carboxyl groups was still too weak, resulting in a low surface hardness. In addition, the ability of these molecules to react with one another was restricted by the low molecular mobility [41]. However, the surface hardness started to increase with increasing epoxy and carboxyl group concentrations because the amount of these groups was sufficient to make the surface harder due to the bonding between the molecules. Consequently, the inherent weakness due to the small sizes of AA and GMA was counterbalanced by their ability to bond with one another.

Fig. 5. Surface hardness as a function of UV dose after UV curing (a), UV and thermal curing (b), thermal curing time (c) and the amount of epoxy and carboxyl group after UV and thermal curing (d).

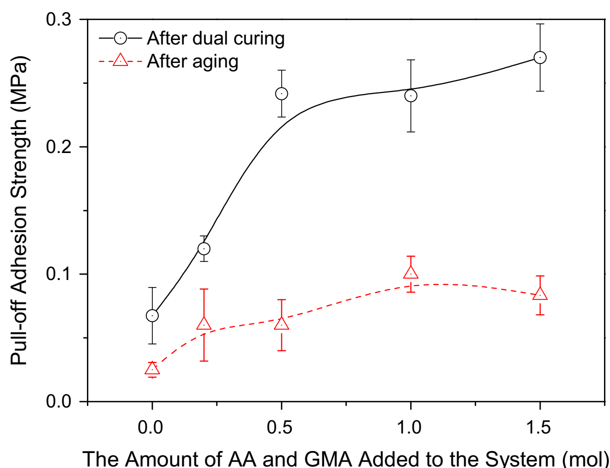

Fig. 6. Adhesion strength after dual curing and aging at 250 °C for 2 h as a function of epoxy and carboxyl functional group content.

3.5. Adhesion strength

As shown in Fig. 6, although adhesion strength increased significantly up to 0.5 mol of epoxy group, it did not change considerably when the amount of epoxy increased from 0.5 mol to 1.5 mol. This effect is due to the reaction between the epoxy and carboxyl groups in the polymer chain, which increased the adhesion strength of the material [32]. Although the surface hardness is high, the adhesion strength of the sample without the epoxy functionalities is the lowest. It is because the brittle properties of the cured film by the greater concentration of the bulky phenyl groups in the polymer backbone compared with the samples containing GMA and AA resulted in poor adhesion strength [25]. When 0.2 mol of epoxy group was added, only a small effect was observed on the adhesion strength. However, upon addition of 0.5 mol of epoxy group, the sample exhibited enough strength to be used at room temperature. The sample with more than 0.5 mol of epoxy exhibited similar adhesion strength due to the limited molecular mobility of the epoxy and carboxyl group because of the crosslinking between the molecules that took place during the UV curing process [41]. Thus, the epoxy and carboxyl group could not react with one another, resulting in lower adhesion strength, despite the fact that the possibility of reaction is higher for these samples than for those containing a lower concentration of epoxy and carbonyl groups.

Current technological applications require adhesives to exhibit high thermal resistance at temperatures greater than 250 °C for at least 2 h without loss of adhesion strength. For example, thin silicone wafers require a temporary bonding process to generate high-quality products. Thus, an aging test was performed at 250 °C to evaluate the thermal stability of the adhesives prepared in this study. In general, the adhesion strength decreased to 1/3 of the initial value and increased with increasing epoxy group

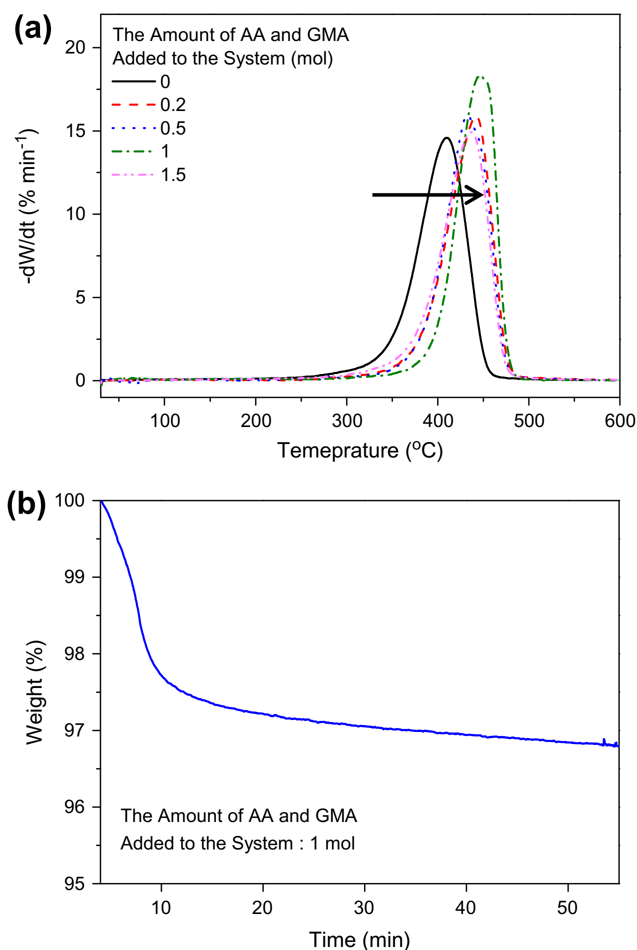

Fig. 7. Derivative thermogram of a dual cured sample as a function of epoxy and carboxyl group content (a) and the weight loss observed for an isothermal treatment at 250 °C (b).

concentration. Despite the decrease in strength, the samples still maintained a certain level of strength such that it was not easy to separate the one substrate from the other substrate. These results demonstrate that the crosslinked structure of the adhesive in this system can withstand high temperatures.

3.6. Thermal gravimetric analysis (TGA)

The derivative of mass loss is provided in Fig. 7a. The peak temperature is related to the temperature of the maximum degradation rate [42]. A degradation peak at approximately 400 °C was observed in the absence of epoxy because the bonding between the epoxy and carboxyl groups did not take place. In contrast, the degradation was delayed in the presence of epoxy and carboxyl groups due to the crosslinking reaction between these groups. Furthermore, with increasing concentrations of epoxy and carboxyl groups, the degradation process becomes further delayed due to the increased crosslinking density [33]. However, a significant difference in the peak temperature was not observed. Under isothermal conditions, approximately a weight loss of 3% was observed at 250 °C over the course of 50 min, as shown in Fig. 7b. This weight loss is related to the approximately 1/3 loss in adhesion strength, as shown in Fig. 6.

4. Conclusion

A series of dual-curable adhesives was prepared by blending bisphenol type A methacrylate, glycidyl methacrylate, acrylic acid, a trifunctional monomer, a photoinitiator and a catalyst. The reaction was performed between these monomers to form a crosslinked structure wherein the epoxy groups reacted with the carboxyl groups in the presence of UV and thermal stimuli. The results were evaluated by FT-IR, gel fraction and pendulum hardness experiments. In the presence of UV irradiation, the reaction heat increased with increasing epoxy and carboxyl group content due to the higher concentration of reactive C=C double bonds. The gel fraction was mainly influenced by the amount of trifunctional monomer introduced for crosslinking. The thermal curing resulted in more bonding between the carboxyl and epoxy groups, leading to a gradual increase in surface hardness. This enhanced bonding also produced improvements in adhesion strength and thermal properties.

Acknowledgement

This study was supported by the Korean Research Council for Industrial Science & Technology in the Republic of Korea.

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