



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 cross-linked 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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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/cm². 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- μ m-thick film prepared by thermally curing for 1 h at 150 °C and then UV curing with a UV dose of 1500 mJ/cm² 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.

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/cm² and a dual-cured film prepared by UV curing with a dose of 1500 mJ/cm² 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 μ m and then either UV curing using 1500 mJ/cm², 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 \pm 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 \pm 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 \times 100 \times 5 (mm³) crosswise and then placing an adhesive between them with a thickness of 20 μ m and an area of 50 \times 50 (mm²). Subsequently, the specimens were cured at 1500 mJ/cm² 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/cm² 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

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

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