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UV- and thermal-curing behaviors of dual-curable adhesives based on epoxy acrylate oligomers

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ABSTRACT

Dual-curable adhesives were prepared using various epoxy acrylate oligomers, a reactive diluent, photoinitiators, a thermal-curing agent and a filler. The UV- and thermal-curing behaviors of the dual-curable adhesives were investigated using photo-differential scanning calorimetry (photo-DSC), Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy, and the determination of the gel fraction, pendulum hardness and adhesion strength.

The reaction rate and extent of UV curing were found to be strongly dependent on the concentration of C=C bonds in the epoxy acrylate oligomers. The FTIR-ATR absorption peak areas representing the relative concentration of C=C bonds in the epoxy acrylate oligomers and trifunctional monomer decreased with increase in UV dose because of photopolymerization. When the dual-curable adhesives were irradiated with UV light, the gel fraction increased with increase in C=C bond contents in the epoxy acrylate oligomers. Also, after thermal curing, the gel fraction was highly enhanced due to the cross-linking reaction of the unreacted glycidyl groups in epoxy acrylate oligomers induced by the thermal-curing agent. This cross-linked structure of the dual-curable adhesives affects the pendulum hardness and adhesion strength.

1. Introduction

Photo-induced reactions comprise polymerization introduced by ultra-violet (UV) light, visible light, electron beam (EB) or laser. Photopolymerization science and technology has attracted a significant amount of attention due to its various industrial applications, such as inks, coatings, photoresists and pressure-sensitive adhesives (PSAs) [1,2]. Among the various methods of photo-curing, UV-curing systems are widely used due to their advantages, such as their rapid production rate in a small place of work, lower process costs, high chemical stability, high dimensional stability and solvent-free curing at ambient temperatures [3,4].

In many industries, epoxy acrylate oligomers, which introduce vinyl ester groups with carbon–carbon double bonds at the end of the epoxy resin, are generally used, because they have excellent adhesive and non-yellowing properties, flexibility, hardness and chemical resistance [5–8]. Also, epoxy acrylate oligomers can be used in a wide rage of viscosities and formulations in the form of single- or two-part products [9]. The epoxy backbone imparts toughness to the cured films, while the carbon–carbon and ether bonds ameliorate their chemical resistance. Their reaction with an acid produces hydroxyl groups, thereby introducing polarity, which can improve the wettability of adhesive [10]. However, acrylic compounds have poor thermomechanical stability, because they generally have a linear structure. Therefore, the cross-linking of functional acrylate oligomers and monomers is needed in order to increase their thermomechanical stability. The advantages of functional acrylates include their good adhesion to plastics, high cross-linking density, reactivity, chemical resistance, and hardness and scratch resistance [11]. Kaczmarek and Decker [12] reported that when an adhesive is weakly cross-linked, it shows a fluid-like behavior; however, in the case of a more highly cross-linked adhesive, the creep resistance is greatly increased [13]. Moreover, functional acrylates crosslink quickly by radical and cationic polymerizations, and their kinetics and properties have previously been investigated [14]. Also, Athawale et al. [15] reported that photopolymerization was effective in obtaining networks with a high degree of interpenetration.

The curing kinetics and peel strength of dual-curable pressure-sensitive adhesives based on acrylic resins were previously reported [16]. Also, Bertoldo et al. [17] investigated the

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polymerization kinetics of dual-cured polyurethane-acrylate nanocomposites. Moreover, various studies of dual-curable materials focused on the interpenetrating network (IPN) structures on coating materials and dental materials [18–20]. In our previous study [21], we synthesized partially acrylated epoxy acrylate oligomers designed for dual-curing and investigated their UV-curing performances. To combine the functionalities of UV and heat curing in an epoxy acrylate oligomer-based system, a thermal-curing agent should be introduced. In recent years, thermally latent curing agents such as dicyandiamide, which exhibit long-term stability at ambient temperature and can be transformed into activated species at high temperatures, have been studied by many researchers in an attempt to obtain epoxy-based resins affording one part handling and good storage stability [22–26]. Also, Chiu et al. [24] used diethylphosphite as a latent curing agent and Zhang et al. [27] investigated chain-extended urea as a latent curing agent. Park et al. [28] reported on the curing behaviors and thermal stability of epoxy resin using the N-benzylpyrazinium hexafluoroantimonate salt (BPH) and the benzyl 2,5-dimethyl pyrazinium hexafluoroantimonate salt (BDPH) as cationic latent curing agents.

In this study, dual-curable adhesives that have various latent curing agent contents were prepared and polymerized by UV irradiation and thermal curing. Their curing behaviors were characterized using photo-DSC, FTIR-ATR spectroscopy, and by determining gel fraction and pendulum hardness (Fig. 1).

2. Experimental

2.1. Materials

A diglycidyl ether of bisphenol A (DGEBA) type epoxy resin (KER 828, epoxy group content: 5260–5420 mmol/kg) was kindly supplied by Kumho P&B Chemicals, South Korea. Acrylic acid (Junsei Chemical, Japan) and triphenylphosphine (TPP, Fluka, Switzerland) were used. Chemical structures of raw materials and prepared epoxy acrylate oligomers are shown in Fig. 2. The trifunctional monomer, trimethylolpropane triacrylate (TMPTA), and two types of photoinitiators, hydroxy cyclohexyl phenyl ketone (Micure CP-4) and hydroxyl dimethyl acetophenone (Micure HP-8), were kindly provided by Miwon Commercial, South Korea. A dicyandiamide-type latent curing agent (Amicure® CG-1400, Air Product) and curing acceleration agent (Sunmide LH-210) were used. Also, hydrophobic fumed silica filler (Aerosil® R 974, Degussa) was used. All reagents were used without any further purification.

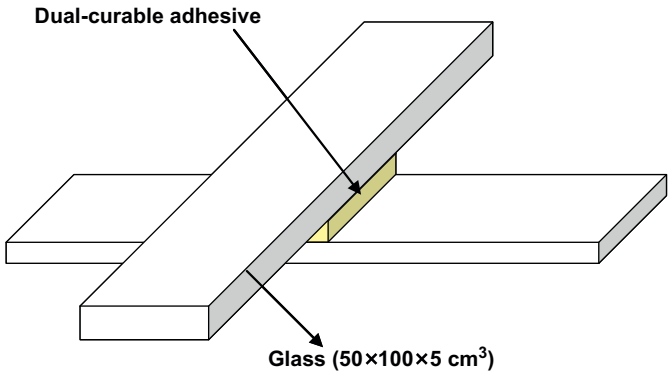

Fig. 1. Schematic diagram of the assembly for the measurement of adhesion strength.

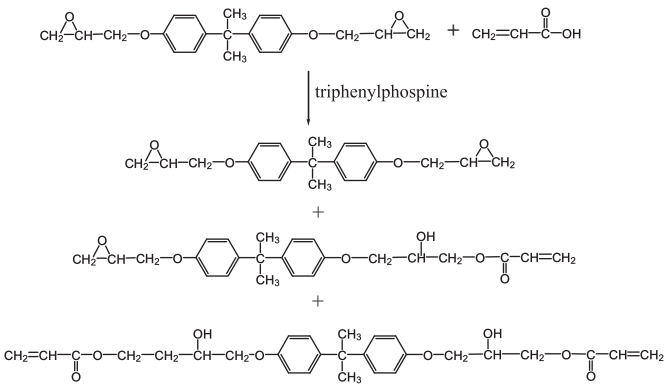

Fig. 2. Synthesis method of epoxy acrylate using epoxy resin and acrylic acid using triphenylphosphine catalyst.

2.2. Preparation of dual-curable adhesives

Epoxy acrylate oligomers having various concentrations of carbon–carbon double (C=C) bonds, TMPTA and photoinitiators were blended first and then latent curing agent, curing acceleration agent and silica filler were mixed using a paste mixer (Daewha Tech, South Korea) at room temperature. The generated heat during mixing was not considered. Table 1 shows the blend ratios of the various dual-curable adhesives. The blending processes were performed in 2 steps to make a homogeneous mixture and to remove the air bubbles in the adhesives. In the first step, the revolution and rotation speed was 1500 rpm for 20 min and then in the second step the revolution speed was 1400 rpm and the rotation speed was 100 rpm for 10 min.

2.3. Curing behaviors

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

Photo-DSC experiments were conducted using a TA Instruments Q-1000 DSC equipped with a photocalorimetric accessory (Novacure 2100 at NICEM, Seoul National University), which used light from a 100 W middle-pressure mercury lamp under nitrogen gas atmosphere. The light intensity was determined by placing an empty DSC pan on the sample cell. The UV light intensity at the sample was 50 mW/cm^2 over the wavelength range of 300–545 nm. The weight of the sample was about 3 mg and the sample was placed in an open aluminum DSC pan with a diameter of about 8 mm. The measurements were carried out at 25 °C.

2.3.2. FTIR-ATR spectroscopy

The IR spectra were recorded using a Nicolet Magna 550 Series II FTIR spectrometer (Midac, USA) equipped with an attenuated total reflectance (ATR) accessory. In order to obtain the IR spectra of the dual-curable adhesives, the cured adhesive samples were cut into $5 \times 0.5\,cm^2$ pieces. The ATR crystal was zinc selenide (ZnSe) and its refractive index at 1000 cm^{-1} was 2.4 with a transmission range from 4000 to 650 cm^{-1}. The resolution of the spectra recorded was 4 cm^{-1}. The curing behavior of the dual-curable adhesives was analyzed by observing the changes in the deformation of the C=C bonds at 1635 cm^{-1}. Also, all FTIR-ATR spectra were modified by means of baseline correction.

2.3.3. Gel fraction

The gel fractions of the dual-curable adhesives after UV curing and subsequent thermal curing at different temperatures, 120 and 150 °C, were determined by soaking in toluene at 50 °C for 1 day. The sample amount was about 5 g. The insoluble part was removed by filtration and dried at 50 °C to a constant weight.

Table 1
Blend ratio of dual-curable adhesives (unit: phr).

Epoxy acrylates oligomers (acrylic acid conc.: 0.2, 0.4, 0.6, 0.8 and 1.0 mol%)	70	70	70	70
TMPTA	30	30	30	30
Photoinitiators (1:1 mixture, 5 phr per TMPTA)	5	5	5	5
Latent curing agent (LCA)	0	10	20	30
Curing acceleration agent (10 phr per LCA)	0	10	10	10
SiO_2	0	10	10	10

The gel fraction was calculated by applying the following equation:

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

where W_0 was the weight before filtration and W_1 was the weight after filtration.

2.3.4. Pendulum hardness

A König pendulum hardness tester (Ref. 707PK, Sheen Instruments Ltd., England) was used to monitor the hardness of the surface for the cured film during the process of UV curing. After its exposure to UV, the pendulum hardness of the UV-cured film surface was measured at $24 \pm 1\,^{\circ}C$ and $50 \pm 2\%$ RH [29].

2.3.5. Shrinkage

To measure the linear shrinkage of the dual-curable adhesives during the UV-curing process, 1 g of the dual-curable adhesives was placed on a circle-shaped stainless steel plate (Φ 20 mm) and then covered with a glass slide ($75 \times 25 \times 1.1\,mm^3$). UV light was irradiated on the assembly for 300 s using a spot curing equipment (SP-7, Ushio, Japan). The average UV light intensity at the sample was approximately $80\,mW/cm^2$ over the wavelength range of 300–545 nm. The displacement of the adhesive sample during the UV curing was recorded by software.

2.4. Adhesion strength

On the glass surface, 0.1 g of the dual-curable adhesives was loaded and crosswise covered with glass ($100 \times 50 \times 5\,mm^3$). These assemblies were cured using a UV-curing equipment with a 100-W high-pressure mercury lamp (Main wavelength: 340 nm). The UV dose used was $1500\,mJ/cm^2$. The UV doses were measured with an IL 390C Light Bug UV radiometer (International Light, Inc., USA). Next, the UV-cured assemblies were cured in a drying oven for 1 h at $120\,^{\circ}C$. The measurements of the adhesion strength were performed at room temperature with a crosshead speed of 2 mm/min.

3. Results and discussion

3.1. Photo-differential scanning calorimetry (photo-DSC)

Photo-DSC offers a simple method of characterizing the UV-curing kinetics for the photopolymerization of UV-cured materials. By monitoring the rate at which heat is released from the photopolymerized sample, the reaction rate can be measured. Therefore, the profiles for the heat of reaction versus time provided by photo-DSC can be used to characterize the photo-induced reaction kinetics and to evaluate the polymerization rate constants [30–32].

Fig. 3 shows the photocalorimetric exotherm (a) and the total area under the thermogram curves (b) for the dual-curable adhesives. All three exotherms show the expected sharp spike-like peak observed immediately on UV exposure, followed by an exponential drop. As reported in our previous study [21], the epoxy acrylate oligomers used contained unreacted epoxy resin and partially acrylated epoxy acrylate oligomer, as well as fully acrylated epoxy acrylate oligomer. Therefore, the various dual-curable adhesives have different curing rates. As shown in Fig. 3(a), the reactivity increased greatly with increase in concentration of C=C bonds in the epoxy acrylate oligomers and the peak height decreased, although their maximum conversions were all the same at 1.2 s. That is, the broadening of the peak indicates that the curing was more spread out and, therefore, a longer time was required for its completion. In addition, the total area under the thermogram curves increased with increase in concentration of C=C bonds, as shown in Fig. 3(b). The dual-curable adhesives showed a higher exothermic area with increase in concentration of C=C bonds in the epoxy acrylate oligomers, due to the increase in the reaction energy [33]. Also, it can be inferred that the increased molecular weight of the epoxy acrylate oligomers with increasing concentration of C=C bonds caused the conversion to decrease due to the entanglement of the epoxy acrylate oligomers.

3.2. FTIR-ATR spectroscopy

The curing kinetics of the photo-induced cross-linking was observed using FTIR-ATR spectroscopy. After the photoinitiation of the dual-curable adhesives by UV irradiation, the specific peaks of the functional monomers or oligomers confirmed that the polymerization was carried out. The curing reaction of the functional acrylate monomers or oligomers can be measured using FTIR spectroscopy because the C=C bonds in the functional monomers take part in the cross-linking reaction by photopolymerization [33]. Before UV irradiation, the absorption bands of the acrylate group (C=C–C=O) are seen at 1635 and $1610\,cm^{-1}$ [34]. Previous research showed that the absorption band at $810\,cm^{-1}$ related to the C=C twisting vibration of the acrylate groups decreases with increase in UV exposure [12,33,35]. These double bonds have a planar conformation, but UV irradiation deforms them into an out-of-plane conformation.

Fig. 4 illustrates the FTIR spectra of the dual-curable adhesives as a function of the UV dose at $1635\,cm^{-1}$. As mentioned above, the C=C bonds of the epoxy acrylate oligomers used in this study react with each other upon prolonged UV exposure and form a tightly cross-linked structure. Therefore, the absorption band at $1635\,cm^{-1}$ was reduced after UV irradiation. The C=O stretching vibration of the acrylate monomers at around $1730\,cm^{-1}$ was adopted as an internal standard band for the calculation required to compensate for the effects of the differences in the thicknesses of the cured dual-curable adhesive samples. The relative concentrations of C=C bonds, as a function of the UV dose, were calculated according to the following equation:

$$\text{Relative concentration of UV cured group}\,(\%) = \frac{[A]^{UV}_{1635}/[A]^{UV}_{1730}}{[A]^{0}_{1635}/[A]^{0}_{1730}} \times 100$$

where $[A]^0_{1635}$ is the IR absorbance at $1635\,cm^{-1}$ before UV irradiation, $[A]^0_{1730}$ the IR absorbance at $1730\,cm^{-1}$ before UV irradiation, $[A]^{UV}_{1635}$ the IR absorbance at $1635\,cm^{-1}$ after UV

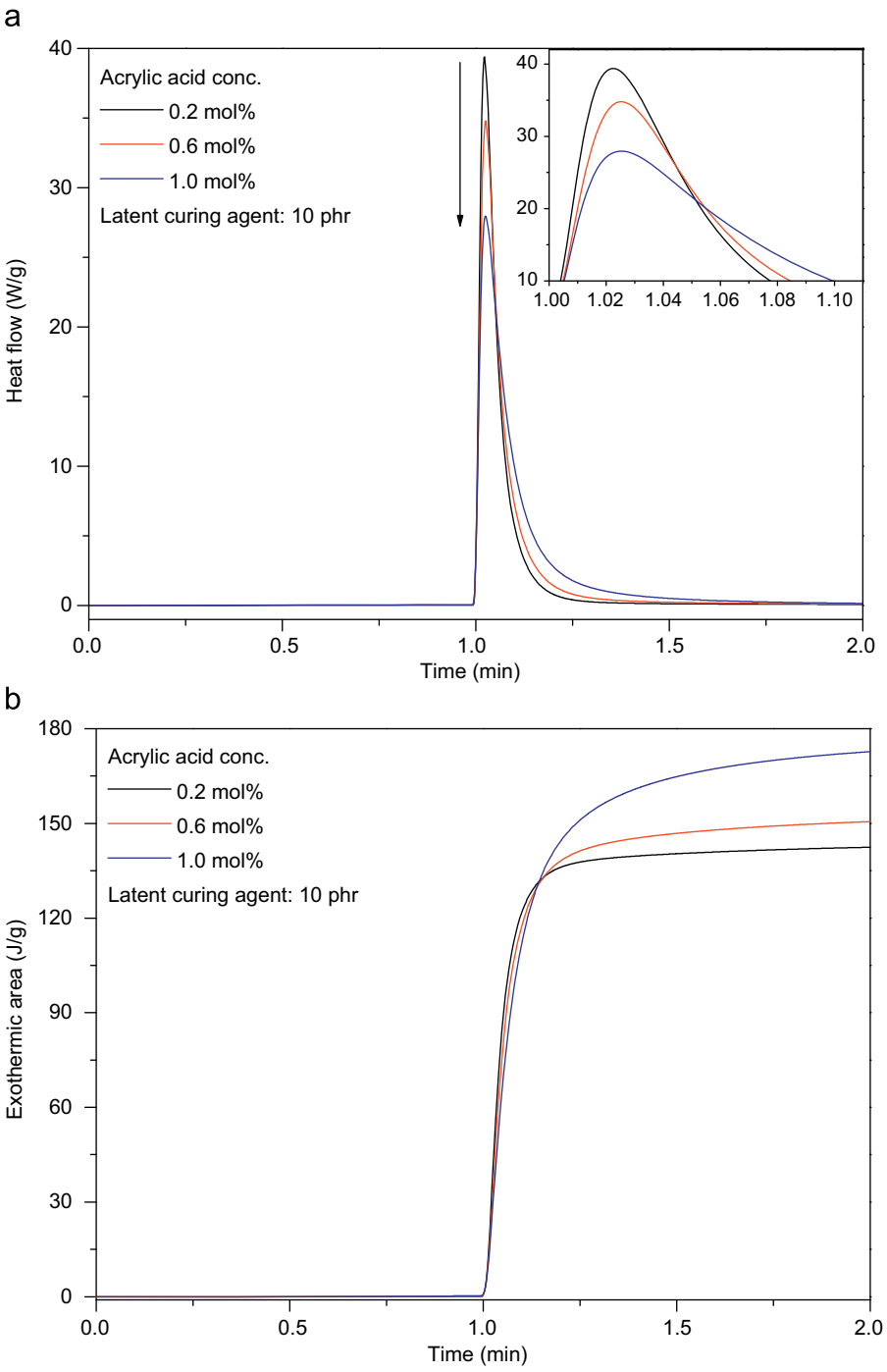

Fig. 3. Photo-DSC thermograms (a) and area under curve (b) of dual-curable adhesives that contain 10 phr of latent curing agent prepared using different concentrations of acrylic acid, viz. 0.2, 0.6 and 1.0 mol%.

irradiation, and $[A]_{1730}^{UV}$ the IR absorbance at 1730 cm^{-1} after UV irradiation.

Fig. 5 shows the relative concentrations of C=C bonds after the UV irradiation of the epoxy acrylate oligomers blended with TMPTA and photoinitiators. As the UV dose is increased, the relative concentration of C=C bonds in the blends sharply decreased, because of the fast reactivity of the trifunctional monomer [33]. In addition, the extent of the decrease in the relative concentration of C=C bonds slightly increased with increase in acrylic acid concentration, because the C=C bond contents were based on the concentration of acrylic acid introduced. Also, the relative concentrations of C=C bonds were not zero. The remaining C=C bonds might have remained unreacted after the action of the photoinitiator because they were trapped in the cross-linked polymer network.

3.3. Gel fraction

Gel fraction determination is a convenient method of measuring the insoluble fractions, such as the fractions of cross-linked or network polymers. In this study, the soluble epoxy acrylate oligomers and trifunctional monomer in organic solvents were turned into insoluble cross-linked structures by photopolymerization.

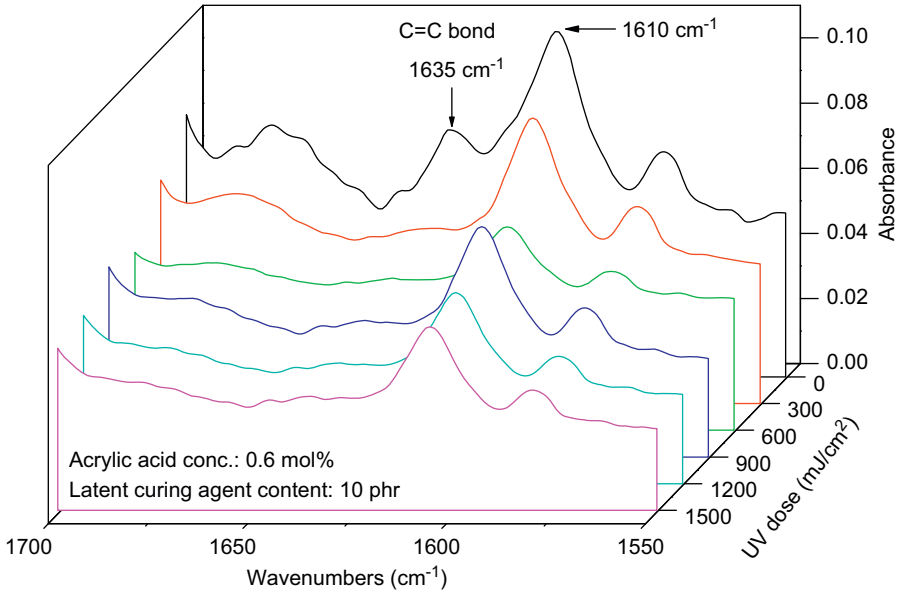

Fig. 4. FTIR-ATR spectra of dual-curable adhesive containing 10 phr of latent curing agent prepared using an acrylic acid concentration of 0.6 mol%, as a function of the UV dose at 1635 cm^{-1}.

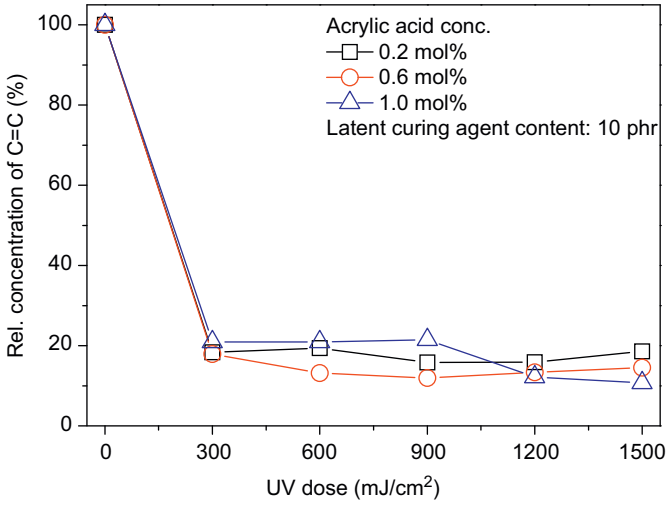

Fig. 5. Relative concentration of C=C bonds at 1635 cm^{-1} as a function of UV dose in dual-curable adhesives that contain 10 phr of latent curing agent prepared using different concentrations of acrylic acid, viz.0.2, 0.6 and 1.0 mol%.

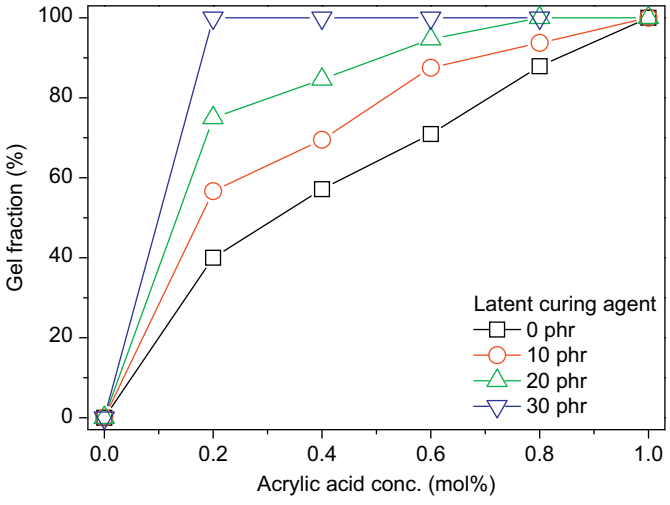

Fig. 6. Gel fraction of dual-curable adhesives after UV curing with a dose of 1500 mJ/cm^2 followed by thermal curing at 120 °C for 1 h.

Fig. 6 shows the gel fraction of the dual-curable adhesives after UV curing with a dose of 1500 mJ/cm^2 followed by thermal curing at 120 °C for 1 h. The gel fraction gradually increased with increase in concentration of acrylic acid used for the end capping of the epoxy resin, because of the increased concentration of C=C bonds in the epoxy acrylate oligomers. Also, the gel fraction increased with increase in thermal-curing agent contents, due to the cross-linking reaction of the unreacted epoxy resin and partially acrylated epoxy acrylate oligomer. At a low concentration of acrylic acid, the gel fraction conspicuously increased, owing to the existence of unreacted epoxy resin, but the rate of increase of the gel fraction decreased with increase in acrylic acid concentration, because the amount of unreacted epoxy resin decreased. When a latent curing agent content of 30 phr was added to the dual-curable adhesives, the gel fraction reached 100% irrespective of the acrylic acid concentration. This means that the unreacted components were encapsulated in the cross-linked structure formed by photopolymerization. Next, during the thermal-curing process, simultaneously, the thermal-curing agent was activated and the glycidyl groups of the unreacted epoxy resin and partially acrylated epoxy acrylate oligomers reacted with each other. Finally, a cross-linked structure similar to a semi-interpenetrating network was formed by all of the components. In order to prove this supposition, the thermal-curing temperature was increased up to 150 °C while keeping the curing time the same.

The gel fraction values of the dual-curable adhesives after UV curing with a dose of 1500 mJ/cm^2 and then thermal curing at 150 °C for 1 h are shown in Fig. 7. The gel fraction gradually increased with increase in acrylic acid concentration, because of the increased C=C bond concentration in the epoxy acrylate oligomers. Moreover, when no thermal-curing agent was added to the dual-curable adhesives, the gel fraction increased due to the cross-linking reaction of the glycidyl groups. Also, the gel fraction of the dual-curable adhesives was increased by the addition of the thermal-curing agent. It reached approximately 100% upon the addition of 20 phr of thermal-curing agent. Therefore, the increase

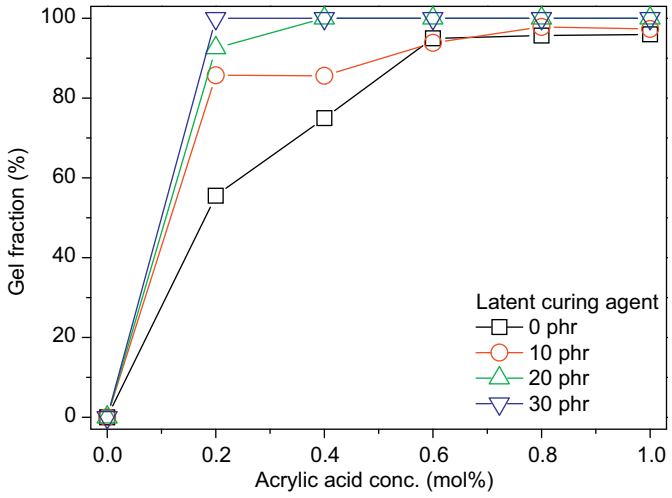

Fig. 7. Gel fraction of dual-curable adhesives after UV curing with a dose of 1500 mJ/cm^2 followed by thermal curing at 150 °C for 1 h.

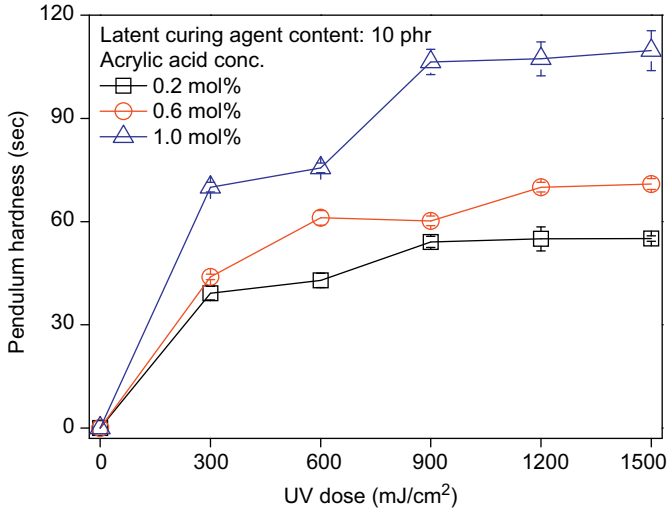

Fig. 8. Pendulum hardness values of the dual-curable adhesives that contain 10 phr of latent curing agent prepared using different concentrations of acrylic acid, viz. 0.2, 0.6 and 1.0 mol%, for various UV doses.

in thermal-curing temperature enhances the effectiveness of the gel fraction and attests to the existence of unreacted epoxy resin molecules in the cross-linked structure of the epoxy acrylate oligomer and trifunctional monomer.

3.4. Pendulum hardness

The pendulum hardness (König hardness) of the dual-curable adhesives as a function of the UV dose is shown in Fig. 8. Before UV irradiation, the pendulum hardness of the dual-curable adhesives cannot be measured, but after UV exposure the dual-curable adhesives form a cross-linked structure and the pendulum hardness is gradually increased. That is, the pendulum hardness is increased with increase in concentration of C=C bonds in the epoxy acrylate oligomers, owing to the tightly cross-linked structure between the oligomer and monomer. Therefore, the pendulum hardness was affected by the concentration of C=C bonds in the oligomer and monomer.

When the UV light is irradiated on the surface of the dual-curable adhesives, the UV-cured film becomes harder and loses most of its rubbery properties. As a result, the stress is increased especially at the surface of the UV-cured film [36,37]. The photo-induced damage causes changes in the chemical composition, besides inducing the cross-linking of the cured film during weathering [39]. This leads to the embrittlement of the UV-cured film. Therefore, the pendulum hardness of the dual-curable adhesives increased with increase in acrylic acid concentration at the same UV dose.

3.5. Shrinkage

Shrinkage and conversion are closely related manifestations of the same process. In general, the rate of contraction is related to the degree of conversion. The general trend is that the volumetric shrinkage increases with increasing degree of conversion. There are many methods of measuring the shrinkage of adhesives [38–40]. In this study, the linear shrinkage of the dual-curable adhesives was measured.

Fig. 9 shows that the typical linear shrinkage of the dual-curable adhesives as a function of time. At the initial stage, the linear shrinkage of the dual-curable adhesives sharply increased with increase in time, but it was stabilized after a prolonged UV dose. After the end of the UV irradiation, the shrinkage slightly increased and then stabilized. Also, the linear shrinkage of the dual-curable adhesives decreased with increase in thermal-curing agent contents. This tendency was conspicuously shown at a thermal-curing agent content of 30 phr. All of the linear shrinkage results are listed in Table 2. When no thermal-curing agent was added to the dual-curable adhesives, somewhat high shrinkage values were observed; however, the shrinkage increased with increase in thermal-curing agent contents in the dual-curable adhesives. Therefore, it can be said that the thermal-curing agent plays the role of a filler in the dual-curable adhesives.

In general, the polymerization shrinkage of the monomers and oligomers is due to the conversion of the intermolecular van-der-Waals forces to covalent single bonds during polymerization [41]. Therefore, as the shrinkage is the consequence of the polymerization reaction, it should follow the pattern of the polymerization reaction.

Consequently, after the UV curing of the dual-curable adhesives, unreacted epoxy resin and partially acrylated epoxy acrylate oligomer remained because some of it was uninitiated or partially initiated by UV exposure. These unreacted resins are initiated by

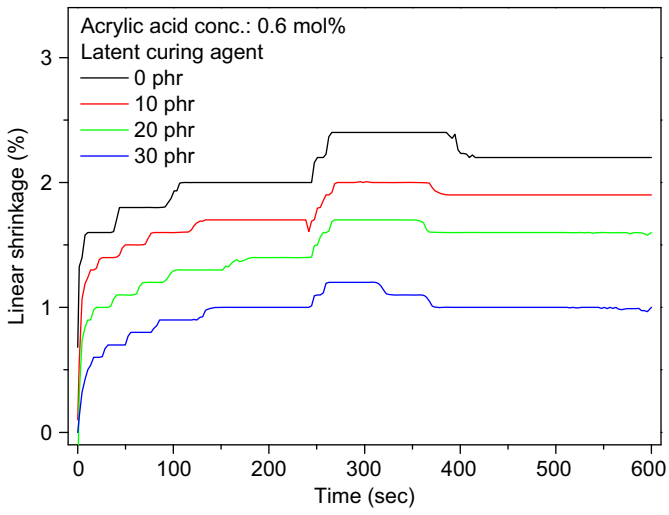

Fig. 9. Linear shrinkage of dual-curable adhesives prepared using epoxy acrylate oligomer reacted with acrylic acid at a concentration of 0.6 mol% and containing various amounts of latent curing agent.

the thermal-curing agent upon the heating of the samples. Fig. 10 shows a schematic diagram of the UV- and thermal-curing process of the dual-curable adhesives.

3.6. Adhesion strength

In order to measure the adhesion strength of the dual-curable adhesives, the dual-curable adhesives were placed between two

Table 2
Linear shrinkage of dual-curable adhesives during UV curing.

Acrylic acid conc. (mol%)	Latent curing agent contents (phr)			
	0	10	20	30
0.2	2.2	1.8	1.7	1.6
0.4	1.9	2.0	1.8	1.5
0.6	2.1	1.9	1.9	1.2
0.8	2.0	1.4	1.4	–
1.0	3.6	1.6	–	–

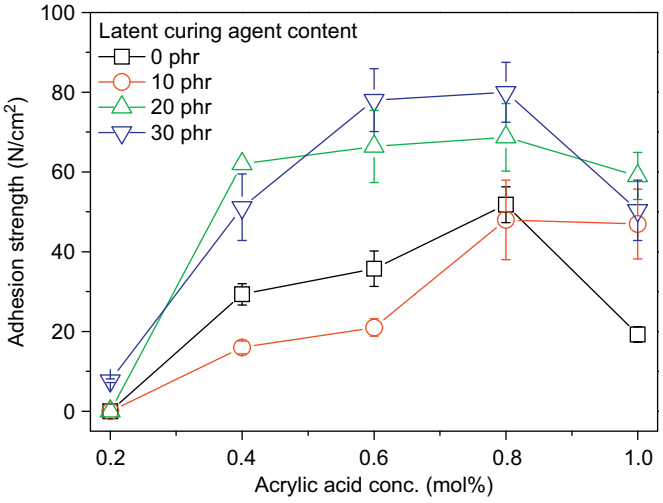

Fig. 11. Adhesion strength of dual-curable adhesives after UV and thermal curing.

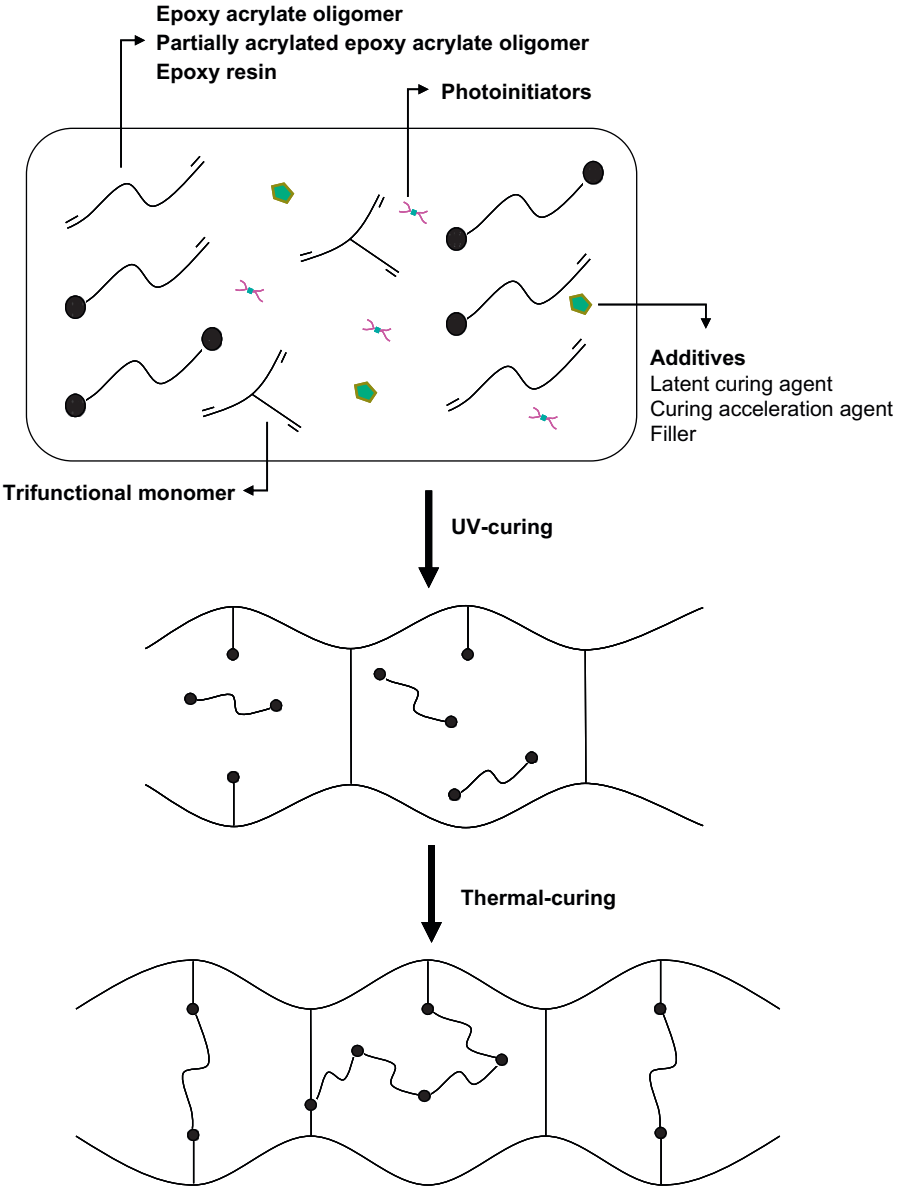

Fig. 10. Schematic diagram of dual-curing mechanism of dual-curable adhesives.

glasses and UV cured with a dose of 1500 mJ/cm^2 and then thermal-cured at 120 °C for 1 h. Fig. 11 shows the adhesion strength of the dual-cured adhesives that have different contents of latent curing agent. When the C=C radical concentration is low, the adhesion strength shows low values, due to the fact that the cross-linking density obtained by UV irradiation is low and unreacted components remain, even though the thermal-curing agent takes part in the thermal-curing reaction. However, the cross-linking density increases with increase in C=C radical concentration, because the thermal-curing agent effectively cures the unreacted epoxy groups. However, the adhesion strength decreases with increase in C=C bond concentration.

4. Conclusions

In summary, we demonstrated the curing behaviors and adhesion strength of dual-curable adhesives prepared by the blending of epoxy acrylate oligomers, a trifunctional monomer, photoinitiators, a thermal-curing agent and a filler. The dual-curable adhesives formed cross-linked structures after UV and thermal curing.

When UV light was irradiated on the dual-curable adhesives, the maximum curing were the same, although the total areas under the thermogram curves were different. That is, the C=C bond contents of the epoxy acrylate oligomers do not affect the curing rate, but they do affect the extent of curing. The FTIR spectra showed a decrease in the intensity of the specific peaks for the C=C bond. Also, the relative concentration of C=C bonds slightly decreased with increase in C=C bond contents. The cross-linked structure of the epoxy acrylate oligomer and trifunctional monomer formed by UV irradiation was tightly cross-linked with increase in C=C bond concentration in the epoxy acrylate oligomer. Therefore, the pendulum hardness increased. Also, the shrinkage of the dual-curable adhesives increased with increase in curing rate, but decreased with increase in thermal-curing agent contents. In addition, the adhesion strength of the dual-curable adhesive samples showed maximum values as the C=C bond contents were increased. The latent curing agent contributed to the enhancement of the adhesion strength.

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