Syntheses and Cured Films Properties of UV-Autocurable BTDA-Based Multiacrylate Resins

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SYNOPSIS

A series of UV-autocurable 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) and benzophenone tetracarboxylic acid (BTAc)-based multiacrylate resins containing pendant glycidyl methacrylate (GMA) or glycidyl acrylate (GA) and 2-hydroxyethyl acrylate (HEA) or 2-hydroxyethyl methacrylate (HEMA) were synthesized. The effects of the acrylic functional groups, the moles of GMA, and the molar ratio of HEMA/HEA on their properties were investigated. The prepared autocurable resins are cured rapidly when exposed to UV or sunlight radiation without addition of any photoinitiator or photosensitizer and the acrylate-type resin resulted in a lower thermal curing temperature and a fast curing rate. Increasing the moles of GMA or the molar ratio of HEMA/HEA on reaction leads to a higher cross-linking density and resulted in film with a higher Young's modulus, breaking strength, and lower elongation. The methacrylate-type resin cured to a very hard, but brittle film with a higher Young's modulus and lower elongation. However, the acrylate-type resin cured to a hard tough film with a lower Young's modulus and higher elongation. The cured methacrylate-type resin results in a lower weight loss at temperature below 300°C due to a higher cross-linking density and lower residual weight percent at 600°C due to the lower percent of benzene rings in the resin. The film properties of the resins coated on steel plates were also investigated.

INTRODUCTION

Many recent studies have been devoted to the UV photopolymerization process, especially the very reactive multifunctional acrylates[1-4] and methacrylates.[5-8] Curing of acrylic oligomers by UV radiation is increasing in industrial importance, in particular, for coating of wood, paper, plastics, and tin plate and for printing ink. UV curing has grown today into a multibilliar dollar industry and has found a large number of applications from protective coatings[9-13] for all kinds of material to photoresists[14,15] for fabrication of microelectronic devices.

However, the relatively large amount of the photoinitiator[16,17] must be included within the system for fast and efficient curing of UV resins. These high levels of photoinitiator will not dissolve or mix homogeneously with the remainder of the certain systems. Even in the systems wherein these large amounts of photoinitiators are compatible, most of the initiator will remain chemically unbounded in the final cured composition, producing deleterious effects on the properties of cured materials. To overcome these disadvantages, many patents[18-21] and articles[22,23] related to oligomers and monomers having built-in photoinitiators, which are autopolymerizable through UV radiation, have been reported. Many patents[24-26] describe complex compounds derived from benzophenone and many articles[27-29] reported the syntheses of UV-autocurable polyester multiacrylate oligomer and the effects of chemical structure, molecular weight, and acrylic functionality on their properties.

In this study, a series of UV-autocurable multiacrylate resins were synthesized. The effects of the acrylic functional groups, the moles of GMA, and

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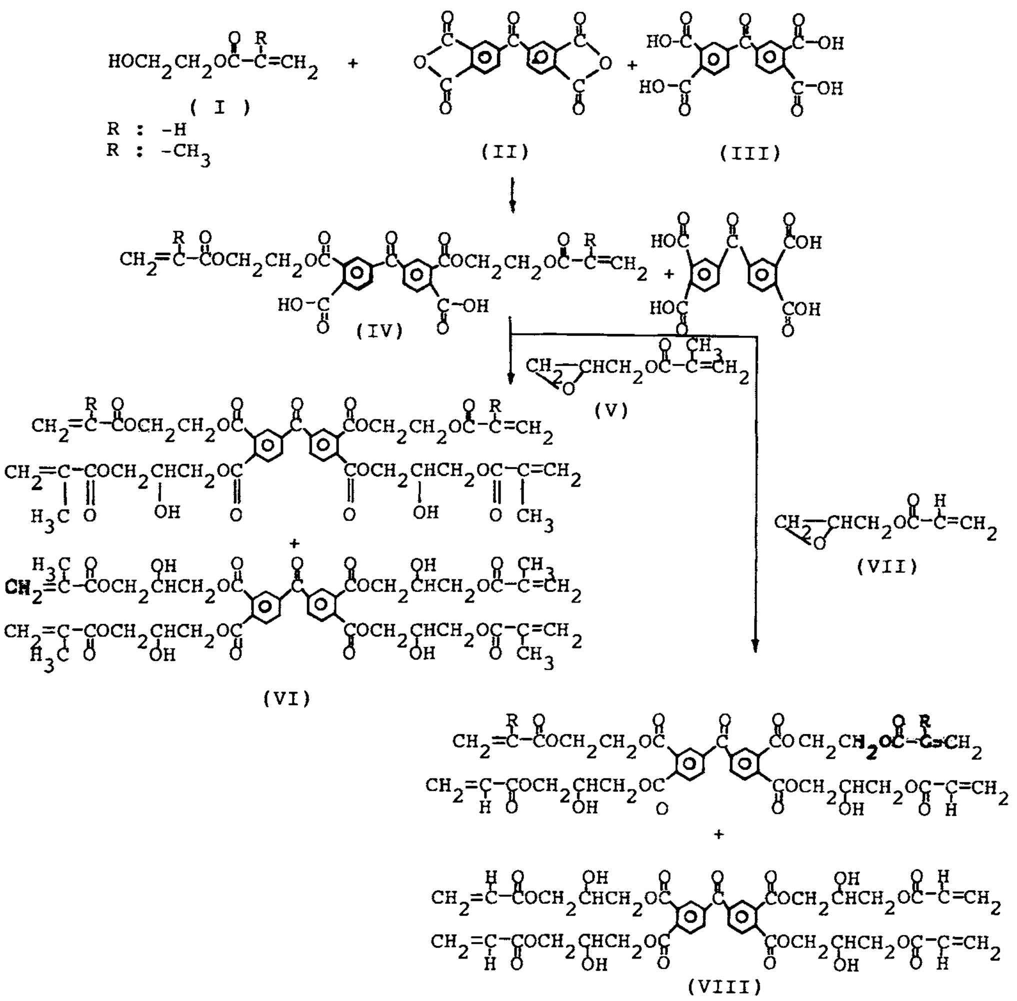
Journal of Applied Polymer Science, Vol. 51, 1901–1911 (1994)
CCC 0021-8995/94/111901-11



Scheme 1 Syntheses of UV-autocurable multiacrylate resins (**VI** and **VIII**). **I**: 2-hydroxyethyl acrylate (or 2-hydroxyethyl methacrylate); **II**: benzophenone tetracarboxylic dianhydride; **III**: benzophenone tetracarboxylic acid; **IV**: half-ester intermediate (BTDA-HEA or BTDA-HEMA); **V**: glycidyl methacrylate; **VII**: glycidyl acrylate.

the molar ratio of HEMA/HEA on their properties are studied. Moreover, the properties of cured films coated on steel plates are also investigated.

EXPERIMENTAL

Materials

3,3′,4,4′-Benzophenone tetracarboxylic dianhydride (BTDA) was purchased from Tokyo Kasei, Japan, and Aldrich Chemical Co., USA. 2-Hydroxyethyl acrylate (HEA), 2-hydroxyethyl methacrylate (HEMA), and glycidyl methacrylate (GMA) were extrapure grade from Tokyo Kasei, Japan. Glycidyl acrylate (GA) was purchased from Aldrich Chemical Co., USA. Dimethyl acetamide (DMAc) was dried by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves and BTDA was dried in a vacuum pump at 80°C for 12 h before use.

Syntheses

UV-Autocurable Multiacrylate Resins (VI)

The autocurable multiacrylate resins were synthesized as shown in Scheme 1. In the first step, into a suitable vessel equipped with means for stirring and temperature control was mixed 0.1 mol of BTDA (containing with benzophenone tetracarboxylic acid [BTAc]) with 0.24 mol of HEA (or HEMA) (prestabilized with *p*-methoxyphenol). The above components were flushed with dry air while heated be-

Table I The Components and Properties of UV-Autocurable Multiacrylate Resins (VI)

	AC2-1	AC3-1	AC4-1	AC5-1	AC2-2	AC3-2	AC4-2	AC4-3	AC4-4
BTDA (mol)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)
HEMA (mol)	(2.4)	(2.4)	(2.4)	(2.4)	(0)	(0)	(0)	(1.8)	(1.2)
HEA (mol)	(0)	(0)	(0)	(0)	(2.4)	(2.4)	(2.4)	(0.6)	(1.2)
GMA (mol)	(2.0)	(3.0)	(4.0)	(5.0)	(2.0)	(3.0)	(4.0)	(4.0)	(4.0)
Acid no. (mg KOH/g)	35.7	12.1	2.3	0.5	28.5	3.3	2.3		
TCT (°C)	149.5	173.4	168.9	165.9	149.8	174.3	179.4	172.3	175.5
Color	All are transparent yellowish brown								
Solubility	Dissolves in acetone, chloroform, dioxane, THF, DMAc, DMSO, DMF, ethyl acetate; insoluble in benzene, toluene, xylene, cyclohexane, MeOH, ether, hexane								

BTDA: 3,3′,4,4′-benzophenone tetracarboxylic dianhydride; HEMA: 2-hydroxyethyl methacrylate; HEA: 2-hydroxyethyl acrylate; GMA: glycidyl methacrylate; TCT: thermal curing temperature of resins determined by DSC.

tween 100 and 105°C for 2.5 h to obtain a half-ester intermediate resin. The completion of the reaction was confirmed by the disappearance of the C=O stretching of the anhydride group at 1860 and 1790 cm^{-1} by IR. After the reaction mixture was cooled to 60°C, GMA (as Table I) was added and the temperature was maintained at 105–110°C for about 2 h.

The chemical structure of the UV-autocurable multiacrylate resins was varied by changing the moles of GMA reacted, the chemical structure (acrylate or methacrylate), and the molar ratio of HEMA/HEA. The chemical compositions of all resins synthesized for this study are listed in Table I.

UV-Autocurable Multiacrylate Resins (VIII)

The autocurable multiacrylate resins were synthesized as shown in Scheme 1. Into a vessel equipped with a thermometer, stirring paddle, dry air purge inlet and outlet, and heater was placed 0.05 mol BTDA (containing with BTAc) and 0.12 mol HEA (or HEMA) (prestabilized with *p*-methoxyphenol). The contents were stirred, then flushed with dried air to inhibit free-radical side reactions while heated between 80 and 90°C for 1 h. After the product was cooled to 60°C, 0.2 mol GA and 4.027 g DMAc (inert solvent, 25 wt % of BTDA) were added and the temperature maintained at 60–70°C for about 1.5 h.

The chemical structure of the UV-autocurable multiacrylate resins was varied by changing the molar ratio of HEMA/HEA. The chemical compositions of all resins synthesized for this study are listed in Table II.

MEASUREMENT OF VARIOUS PROPERTIES

The characterization methods and curing process were performed according to previous studies[27–29];

Table II The Components and Properties of UV-Autocurable Multiacrylate Resins (VIII)

	WT2-1	WT2-4	WT2-3	WT2-2
BTDA (mol)	(1.0)	(1.0)	(1.0)	(1.0)
HEMA (mol)	(2.4)	(1.2)	(0.6)	(0)
HEA (mol)	(0)	(1.2)	(1.8)	(2.4)
GA (mol)	(4.0)	(4.0)	(4.0)	(4.0)
Acid no. (mg KOH/g)	7.67	8.34	7.79	8.52
TCT (°C)	150.58			149.28
Color	All are transparent yellowish orange			
Solubility	Dissolves in acetone, dixoane, THF, DMAc, DMSO, DMF, benzene; insoluble in toluene, xylene, ethyl acetate, chloroform, cyclohexane, MeOH, ether, hexane			

GA: glycidyl acrylate. See footnote to Table I for other abbreviations.

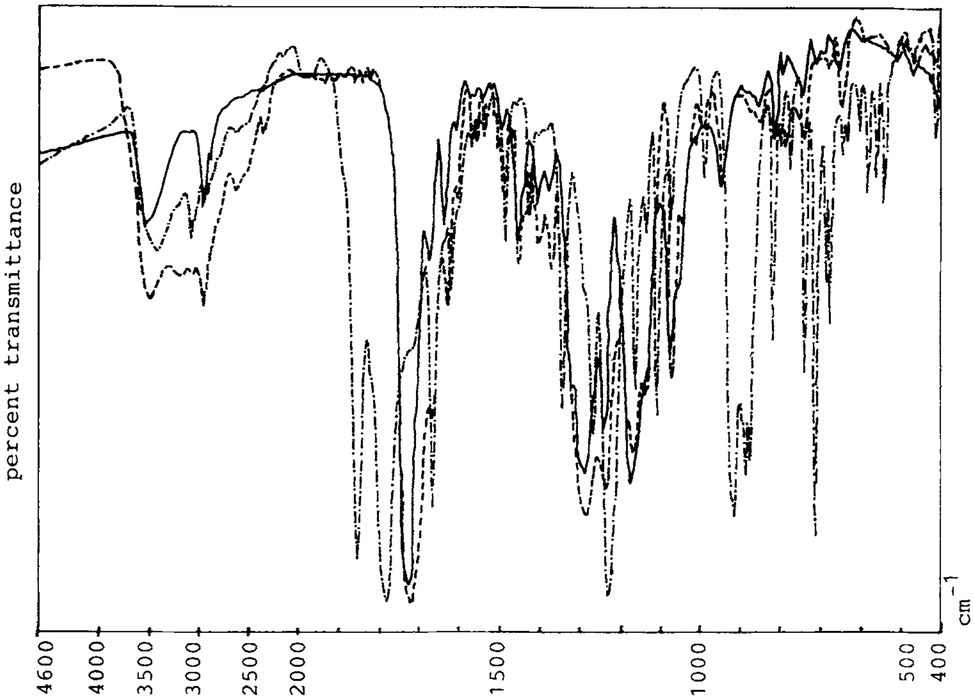


Figure 1 IR spectra of UV-autocurable multiacrylate resins: (——) AC4-1, (BTDA–HEMA, – – –) half-ester intermediate, and BTDA (– • –).

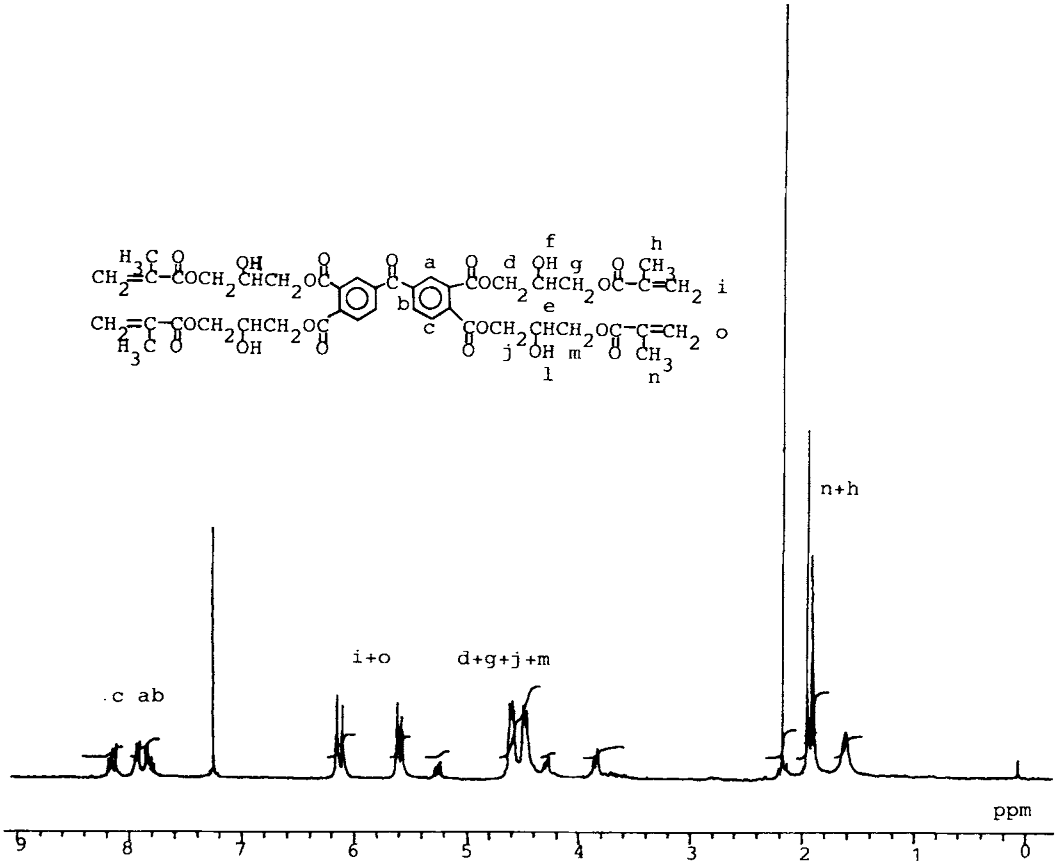


Figure 2 ^{1}H-NMR spectra of UV-autocurable multiacrylate resin (AC5-1).

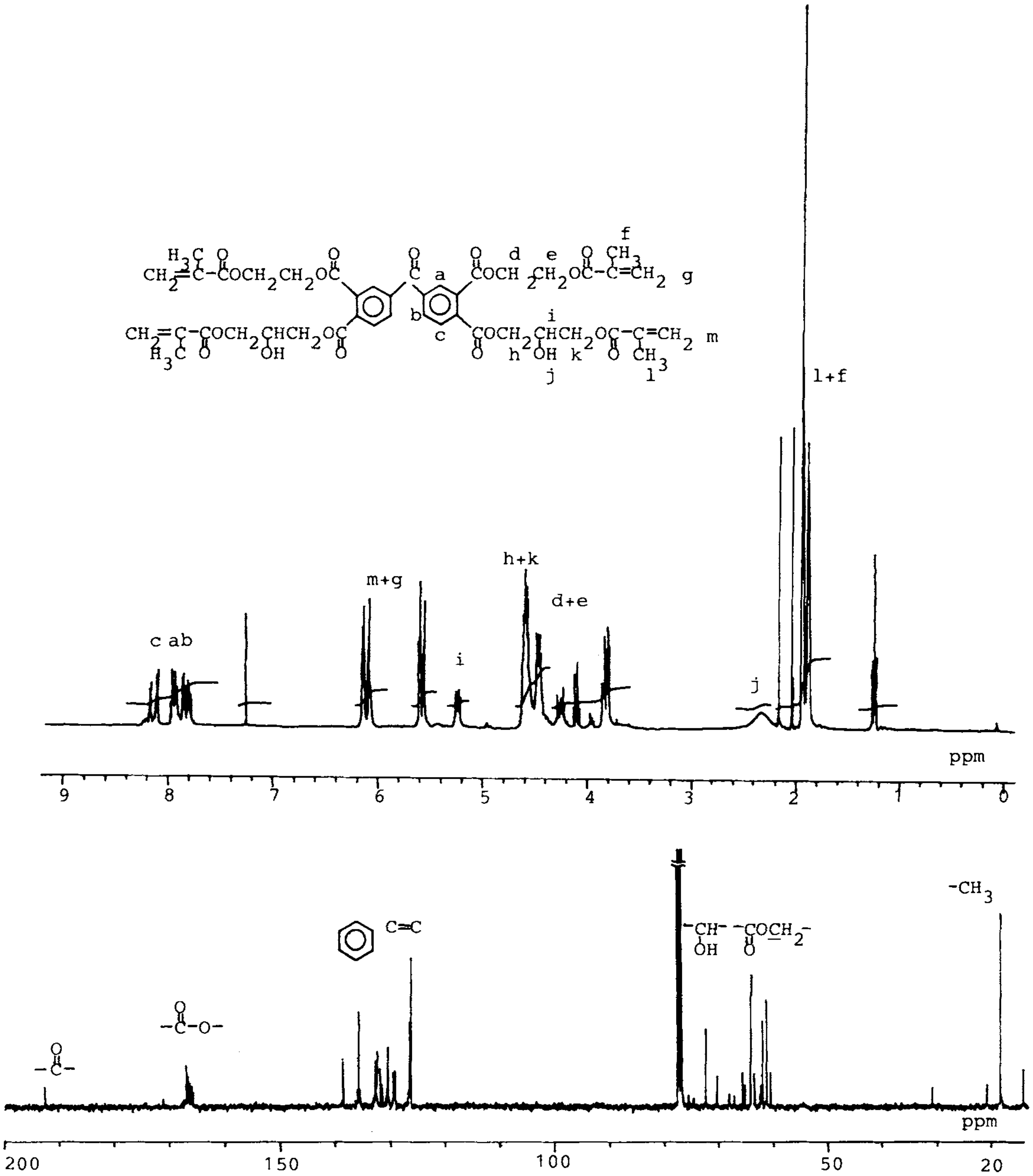


Figure 3 ^{1}H-NMR and ^{13}C-NMR spectra of UV-autocurable multiacrylate resin (AC5-1).

IR spectra of resins were obtained on a JASCO FT/IR 7000. The analysis of ^{1}H-NMR and ^{13}C-NMR were obtained on a JEOLEX-400 MHz FT-NMR. The chemical shift (δ) was given in ppm with tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as a solvent. The DuPont 910 differential scanning calorimeter was used to obtain the initial curing temperature. The decomposition temperature of UV-curable films was also obtained using a DuPont 951 thermogravimetric analyzer at a heating rate of 20°C/min and a test range of 50–600°C under a nitrogen purge.

Prepared resins were cast between two Mylar films and irradiated by a high-pressure mercury lamp (Model USH-500D manufactured by Ushio Electric Co., Japan) to obtain cured films of about 0.2 mm in thickness. Tensile testing was run at 25°C using a Instron Testing Machine (Model 1130) with a crosshead speed of 5 cm/min and a gauge length of 20 mm.

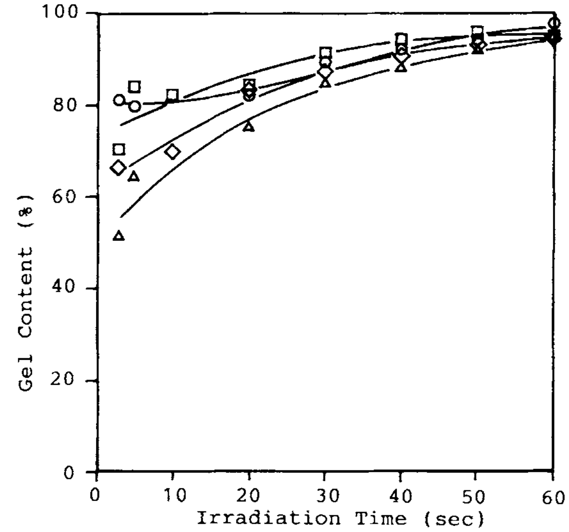


Figure 4 Gel content of cured resins as function of UV-irradiation time: (△) AC2-1; (□) AC3-1; (○) AC4-1; (◇) AC5-1.

RESULTS AND DISCUSSION

Syntheses and Characterization of UV-Autocurable Multiacrylate Resins

The synthetic reaction has been described in the preceding sections. Scheme 1 summarizes these reactions and Tables I and II show the chemical composition of each resin synthesized. The structure of the BTDA (and BTAc)-based multiacrylate resins was varied by changing the moles of GMA and the molar ratio of HEMA/HEA reacted. The addition reaction of BTDA (BTAc) and HEA (HEMA) was carried out to give the half-ester intermediate resin. The IR spectrum of the half-ester intermediate is illustrated in Figure 1. The IR spectrum of the product mixture showed that the anhydride characteristic absorption peaks of BTDA at 1860 and 1790 cm^{-1} completely disappeared, but the acid value was decreased only from 314 to 237 mg KOH/g, indicating that about 50% of the BTDA anhydride groups were opened to acid groups before the addition reaction occurred.

Furthermore, the spectrum showed an appearance of OH stretching at 3528 cm^{-1} due to the excess of HEA (or HEMA) monomer, $C{=}C$ stretching at 1636 cm^{-1}, $C{=}O$ stretching of the ester group at 1730 cm^{-1}, and $C{=}O$ stretching of the benzophenone group at 1670 cm^{-1}. The excess of the HEA (or HEMA) monomer plays the role of a reactive diluent during the reaction. The IR spectrum of the multiacrylate resin showed that the absorption peak of the epoxide group at 910 cm^{-1} completely disappeared and an appearance of OH stretching at 3528 cm^{-1} due to the ring-opening reaction of epoxide and acid group. The acid values of resins were shown in Tables I and II.

In multiacrylate resins (**VIII**), 25% by weight of BTDA of an inert polar solvent DMAc is helpful in dissolving the components and does not interfere with subsequent reactions or with curing by UV light. Usually, the solvent needs not be removed from the final product.[24]

Figures 2 and 3 show the ^{1}H-NMR and ^{13}C-NMR spectra of the UV-autocurable multiacrylate resin (AC5-1). The analytical sample was obtained by chromatography on a silica-gel column using ethyl acetate/hexane as eluent.

Influence of the Amount of GMA and Molar Ratios of HEMA/HEA on Pot Life and Curing Rate of Multiacrylate Resins

The Multiacrylate Resins (VI)

All thermal curing temperatures of resins are above 149°C as heat is liberated by the cross-linking reaction and increase with increasing moles of GMA reacted due to the lower concentration of benzophenone groups. In the multiacrylate resins prepared with a constant amount of HEA (or HEMA), the UV or sunlight curing rate increased with increasing moles of GMA reacted at first and then decreased with increasing moles of GMA reacted, as shown in

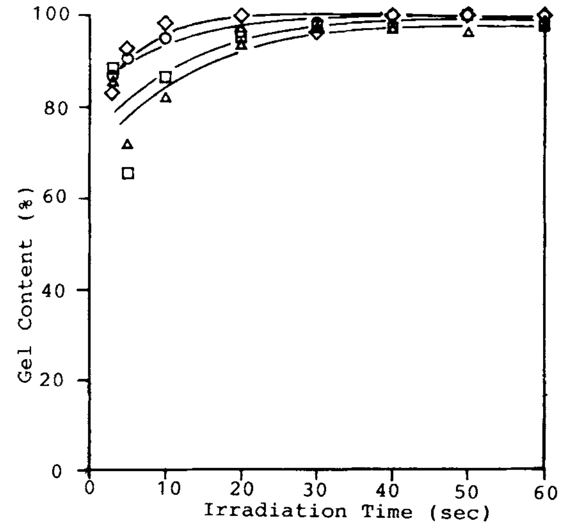


Figure 5 Gel content of cured resins as function of UV-irradiation time: (△) WT2-1; (□) WT2-4; (○) WT2-3; (◇) WT2-2.

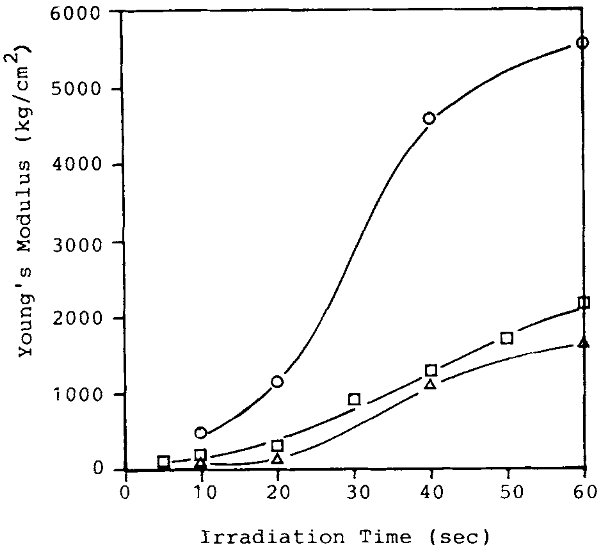


Figure 6 Young's modulus of cured resins as function of UV-irradiation time: (△) AC2-2; (□) AC3-2; (○) AC4-2.

Figure 4. This result is attributed to the higher acrylic functionality of resins at first but then decreasing the degree of benzophenone C=O groups. The UV polymerization of all resins in this study proceeded readily with increasing irradiation time.

All thermal curing temperatures of resins are above 168°C as occurring gelation and decrease with increasing molar ratios of HEMA/HEA reacted. This result is attributed to the different chemical structure between methacrylic and acrylic groups.

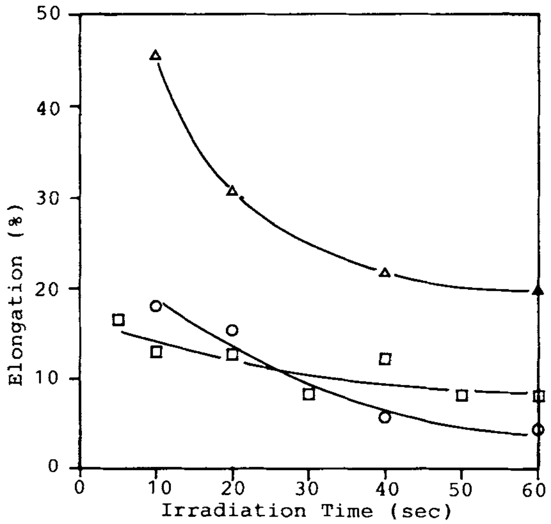


Figure 7 Elongation at break of cured resins as function of UV-irradiation time: (△) AC2-2; (□) AC3-2; (○) AC4-2.

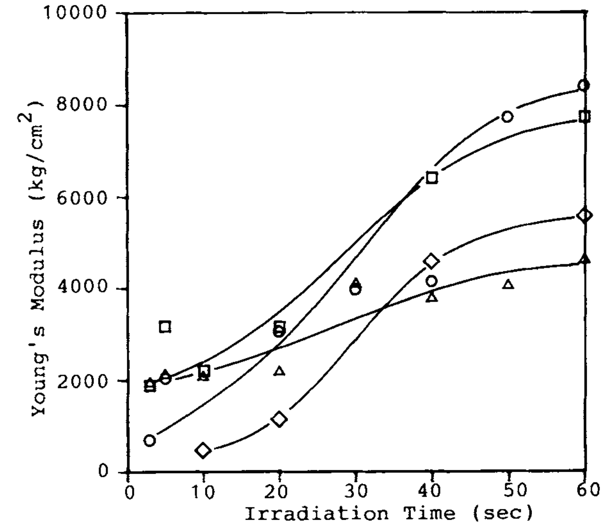


Figure 8 Young's modulus of cured resins as function of UV-irradiation time: (△) AC4-1; (□) AC4-3; (○) AC4-4; (◇) AC4-2.

The UV curing rate increases with the increasing molar ratio of HEMA/HEA reacted. This result is also attributed to the different chemical structure between acrylic and methacrylic groups. The obtained film cured by UV irradiation for only 3 s can have a gel content of 82%.

The Multiacrylate Resins (VIII)

Gelation of all resins are below 150°C and increase with an increasing molar ratio of HEMA/HEA re-

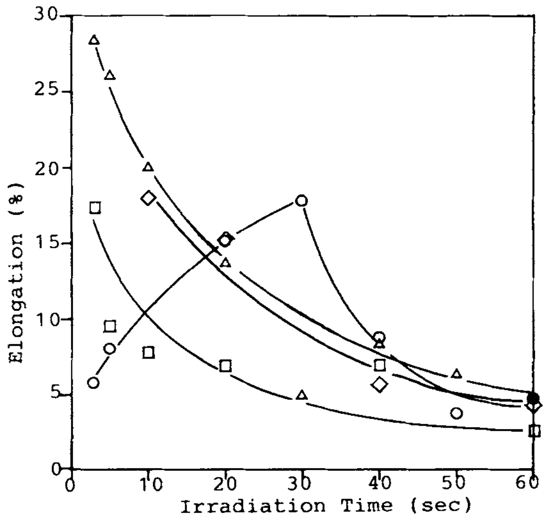


Figure 9 Elongation at break of resins as UV-irradiation time: (△) AC4-1; (□) AC4-3; (○) AC4-4; (◇) AC4-2.

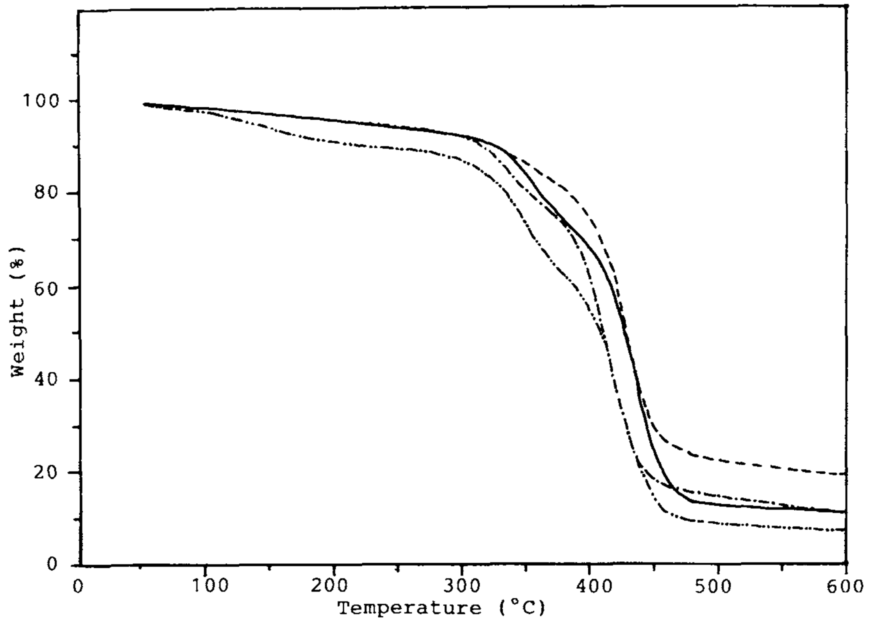


Figure 10 TGA of cured films with various molar amounts of glycidyl methacrylate: (– – –) AC2-1; (– • –) AC3-1; (——) AC4-1; (– • • –) AC5-1.

acted. The UV curing rate decreases with an increasing molar ratio of HEMA/HEA reacted, as shown in Figure 5. The results are attributed to the fact that the curing rate of the acrylic functionality is faster than that of the methacrylic functionality. The obtained WT2-2 film cured by UV irradiation for only 5 s can have a gel content of 93%.

Influence of the Amount of GMA and Molar Ratios of HEMA/HEA on the Tensile Properties of Cured Films

The Multiacrylate Resins (VI)

Increasing moles of GMA reacted leads to an increase in the methacrylic functionality of resins and in the cross-linking density of cured films. As shown in Figures 6 and 7, an increase of cross-linking density would be expected to give rise to a higher Young's modulus, breaking strength, and lower elongation at break. As shown in Figures 8 and 9, the cured AC4-3 (molar ratio of HEMA to HEA is 3 to 1) and AC4-4 (molar ratio of HEMA to HEA is 1 to 1) resins show brittleness with a higher Young's modulus and elongation at break.

The Multiacrylate Resins (VIII)

The tensile properties of cured systems are related to cross-linking density. The Young's modulus and the breaking strength of cured films increased with increasing molar ratio of HEMA/HEA reacted, while the elongation at break decreased.

The cured WT2-1 (reacted with 100 mol % HEMA) resin shows hard and brittle properties with the highest Young's modulus, breaking strength, and the lowest elongation. However, the cured WT2-2 (reacted with 100 mol % HEA) resin exhibit soft

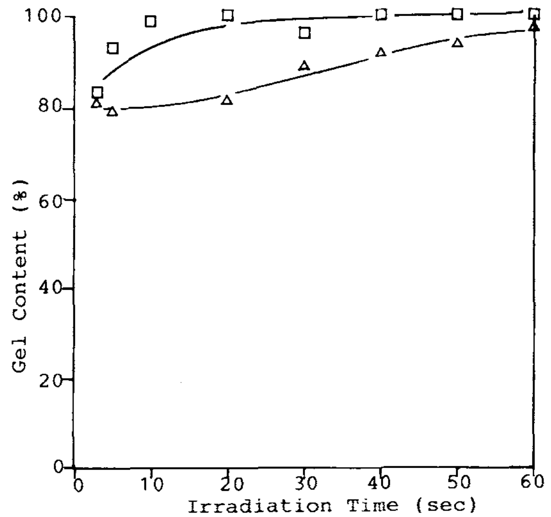


Figure 11 Gel content of cured resins as function of UV-irradiation time: (△) multimethacrylate type; (□) multiacrylate type.

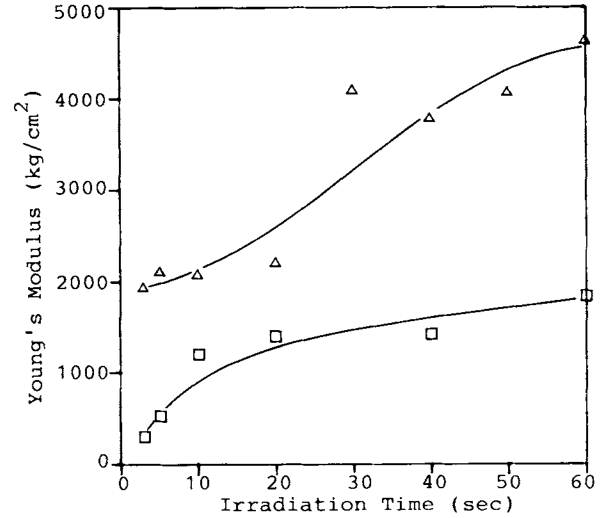


Figure 12 Young's modulus of cured resins as function of UV-irradiation time: (□) multiacrylate type; (△) multimethacrylate type.

and tough properties with the lowest Young's modulus, breaking strength, and the highest elongation at break.

Influence of the Amount of GMA and Molar Ratios of HEMA/HEA on the Thermal Properties of Cured Films

The thermal stability of cured films will be a function of cross-linking density. Increasing moles of GMA reacted results in a lower weight loss at temperatures below 300°C and the residual weight percent of cured resins at 600°C decreases with increasing moles of GMA reacted, as shown in Figure 10. This result is attributed to the lower amount of benzene rings in the resins. All cured oligomers begin to decompose above 313°C. The residual weight percent of cured resins at 600°C decreases with increasing molar ratio of HEMA/HEA reacted. This result is attributed to the lower amount of benzene rings in the resins. The DSC curves of the cured films showed two exothermic decomposition peaks. The residual weight percent at 600°C of WT2-1 is lower than that of WT2-2 due to the lower amount of benzene rings in the resins.

Influence of the Acrylate Type on the Properties of Cured Films

Pot Life and Curing Rate

The thermal curing temperature of the acrylic functional group-type resin was lower than that of methacrylic functional group-type resin. Figure 11 shows the UV curing rate of cured films as affected by the functional group types. The acrylic functional group-type resin resulted in a fast curing rate. This result is attributed to the fact that acrylates cure at extremely rapid rates compared to other monomer systems.

Tensile Properties

Figures 12 and 13 show that tensile properties of cured films are affected by the functional group types. The acrylic functional group type resin was cured to a hard tough film and the methacrylate resin was cured to a very hard, brittle film. Hence, the cured methacrylate resins exhibit brittle properties with higher Young's modulus and lower elongation due to a higher cross-linking density and the cured acrylate resin shows tough properties with lower Young's modulus and higher elongation.

Thermal Properties

The TGA curve of cured resins as affected by the functional group types reacted is shown in Figure 14. The cured methacrylate resins lost less weight before 300°C and left less residual weight up to 600°C. These results are attributed to the higher cross-linking density and the lower percent of benzene rings in the resin. The DSC curves of the cured films showed two exothermic decomposition peaks.

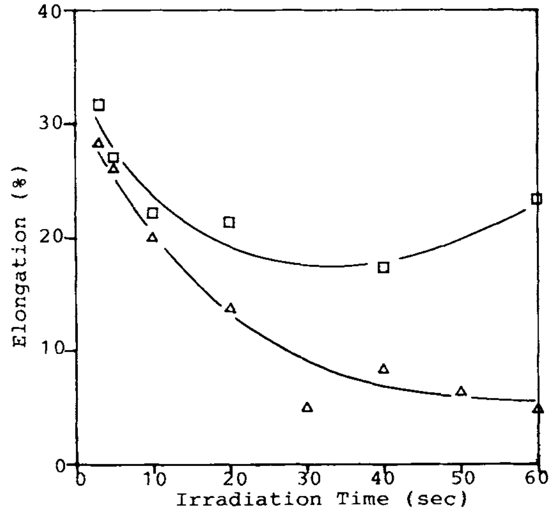


Figure 13 Elongation at break of cured resins as function of UV-irradiation time: (□) multiacrylate type; (△) multimethacrylate type.

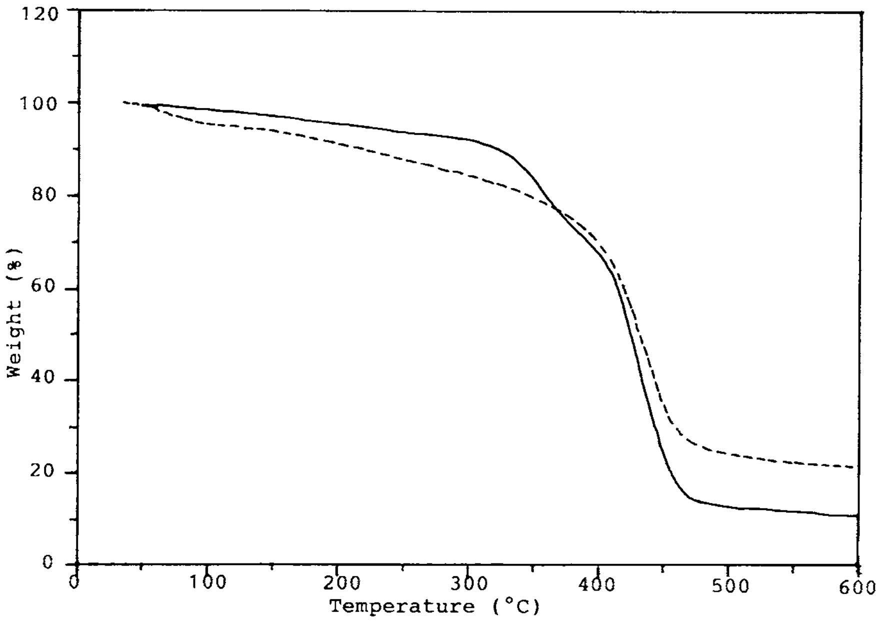


Figure 14 TGA of cured films at nitrogen atmosphere: (——) multimethacrylate type; (– – –) multiacrylate type.

Coating Properties

The values of performance properties of multiacrylate resin coated on steel plates are collected in Table III. The cured coating shows the excellent results, except the resistance to alkali corrosion. The poor resistance of coatings toward alkali is due to hydrolysis of the ester group in the resin.

CONCLUSION

The UV-autocurable BTDA (BTAc)-based multiacrylate resins are synthesized via a series of addition reaction and their chemical structures are varied by changing the moles of GMA reacted, the molar ratio of HEMA/HEA, and the acrylic functional groups. The obtained autocurable resins are cured rapidly when exposed to UV or sunlight radiation without adding any photoinitiator or photosensitizer. Increasing moles of GMA reacted leads to an increase in methacrylic functionality of resins and cross-linking density of cured films and a decrease in acid value. These results are reflected in an increased Young's modulus and breaking strength but a decreased elongation at break. The UV or sunlight curing rate increased with increasing the moles of GMA reacted at first and then decreased. For the multiacrylate resins (**VI**), the UV curing rate increases with increasing molar ratio of HEMA/HEA reacted. Among prepared multiacrylate resins, for instance, the cured AC4-3 and AC4-4 resins have higher Young's modulus, breaking strength, and lower elongation. For the multiacrylate resins

Table III Coating Properties of Cured Multimethacrylate and Multiacrylate Resins

	AC4-1	AC4-2	WT2-1	WT2-2
Hardness[a]	4H	4H	3H	3H
Adhesion	100/100	100/100	100/100	98/100
Acid corrosion test 5% HCl, 72 h	OK	OK	OK	OK
3% acetic acid, 72 h	OK	OK	OK	OK
Salt corrosion test 5% NaCl, 72 h	OK	OK	OK	OK
Alkali corrosion test 1% NaOH, 72 h	OK	OK	Fail	Fail

[a] Hardness is determined as a measure of surface hardness according to ASTM-D3363-74 (reapproved 1989).

(**VIII**), the UV curing rate decreases with increasing molar ratio of HEMA/HEA reacted. Increasing molar ratio of HEMA/HEA reacted leads to a higher cross-linking density, making cured film with higher Young's modulus, breaking strength, and lower elongation at break. The thermal curing temperature of the acrylate-type resin was lower than that of the methacrylate-type resin and the acrylate-type resin resulted in a fast curing rate. The methacrylate-type resin was cured to a very hard, brittle film with a higher Young's modulus and lower elongation due to a higher cross-linking density. However, the acrylate-type resin was cured to a hard tough film with a lower Young's modulus and higher elongation. The cured methacrylate-type resins that showed lower weight loss before 300°C had left a lower residual weight up to 600°C. The poor resistance of coatings toward alkali is due to hydrolysis of ester group in the resin.

The authors wish to express their gratitude to Dr. T. S. Lin, the President of the Tatung Institute of Technology. Thanks are due to Dr. Nobuo Nakabayashi, Professor at the Institute for Medical and Dental Engineering, Tokyo Medical and Dental University, as well as to the Rotary Yoneyama Memorial Foundation, Inc., for their kindness, encouragement, and support.

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Received July 26, 1993
Accepted September 15, 1993