

Synthesis and Properties of Ultraviolet-Curable Resins via a Thio-Ene (Thiol and Allyl) Addition Reaction

Wen-Yen Chiang, Fan-Chun Ding

Department of Chemical Engineering, Tatung University, Taipei, 10451, Taiwan, Republic of China

Received 8 June 2001; accepted 20 December 2001

ABSTRACT: Benzophenone diallyl ester (**I**) and benzophenone tetraallyl ester (**II**) based on 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) with allyl alcohol (AAL) were synthesized. Glycidyl methacrylate (GMA) was added to **I** and formed diallyl diglycidyl methacrylate (**III**). These BTDA-based allyl-containing compounds (**II** and **III**) reacted with 1,4-butanedithiol and 4,4'-thiol-bisbenzenethiol to produce ultraviolet (UV)-curable resins via a thio-ene addition reaction. The ester (**III**) was cured easily when exposed to UV or sunlight radiation without any photoinitiator and only required a lower thermal curing temperature. The diallyl ester (**I**) and tetraallyl ester (**II**) required the

addition of benzophenone to increase the photosensitivity, which reduced the exposition time. These resins used AAL as a monomer to successfully reduce the oxygen effect of the photocuring. The resin BTDA-2Allyl-2GMA had a glass-transition temperature of 166°C and a hardness of 6H. The resultant UV-curable coatings had excellent hardness, chemical resistance, adhesion, and tensile properties. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1878–1885, 2002

Key words: UV-curable resin; thio-ene addition reaction; diallyl diglycidyl methacrylate; coating

INTRODUCTION

With the demands for low pollution, conservation of resources, and reduction of energy consumption in industry, nonsolvent resins have been widely used for coatings, painting, adhesion, and insulation in recent years. In other words, high-intensive radiation energy such as ultraviolet (UV) and electron-beam radiation has been developed to alter conventional thermal processes. There are a great number of articles and patents on photocurable resins, including unsaturated polyester, epoxy acrylate, acrylate or methacrylate, and urethane types.¹ An ever growing number of resins that polymerize readily under UV radiation, particularly the very reactive multifunctional acrylates^{1–4} and methacrylates,^{5–8} began to be commercialized when the many advantages of this new technology^{9–12} became apparent. Acrylic oligomer curing with UV radiation is increasing in industrial importance, particularly for coatings of wood, paper, plastics, and tin plates for printing ink. UV curing has grown today into a multibillion dollar industry and has found a large number of applications, from protective coatings^{13–17} for all kinds of materials to photoresists^{18,19} for the fabrication of microelectronic devices.

The addition of thiols to olefins to form thioesters is a reaction that has been extensively studied since its discovery by Posner in 1905.²⁰ In 1977, researchers at W. R. Grace Co.²¹ studied the mechanism of ketone-sensitized thio-ene addition and proposed that the photosensitized crosslinking of polymers with polythiols occurred as a result of a free-radical chain mechanism. In addition, 3M Co.²² introduced a new system that cured photochemically with a cationic mechanism. UV curing has been widely applied in industry for coatings and painting inks²³ for which an extremely high degree of cured film extensibility is not necessarily required in most cases. In the coating industry, the cured film must provide high reactivity, better adhesive ability, and ideal impact strength. In addition, special extensibility is particularly needed. There are two style additions for the thio-ene system. The first is the backbone thio-ene addition associated with polythiols and polyenes through network crosslinking. The second is the branch thio-ene addition associated with the Markovnikov rule and anti-Markovnikov rule.^{24,25}

Detailed investigations into photocurable resins with thio-ene addition agents have not been reported. This study investigated the synthesis of resins with two kinds of curable agents that could create new applications for photocurable resins.

EXPERIMENTAL

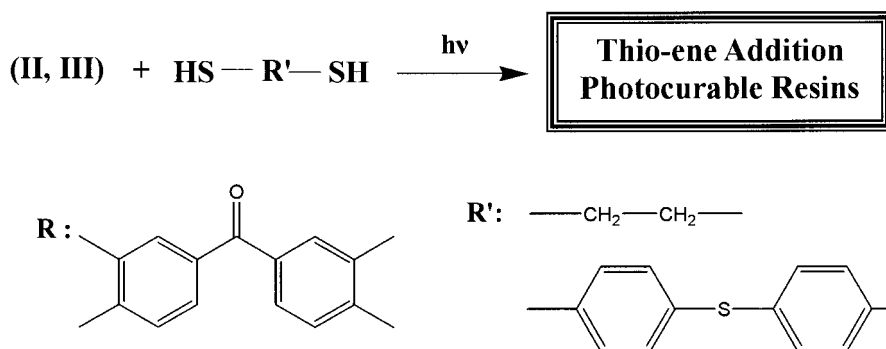
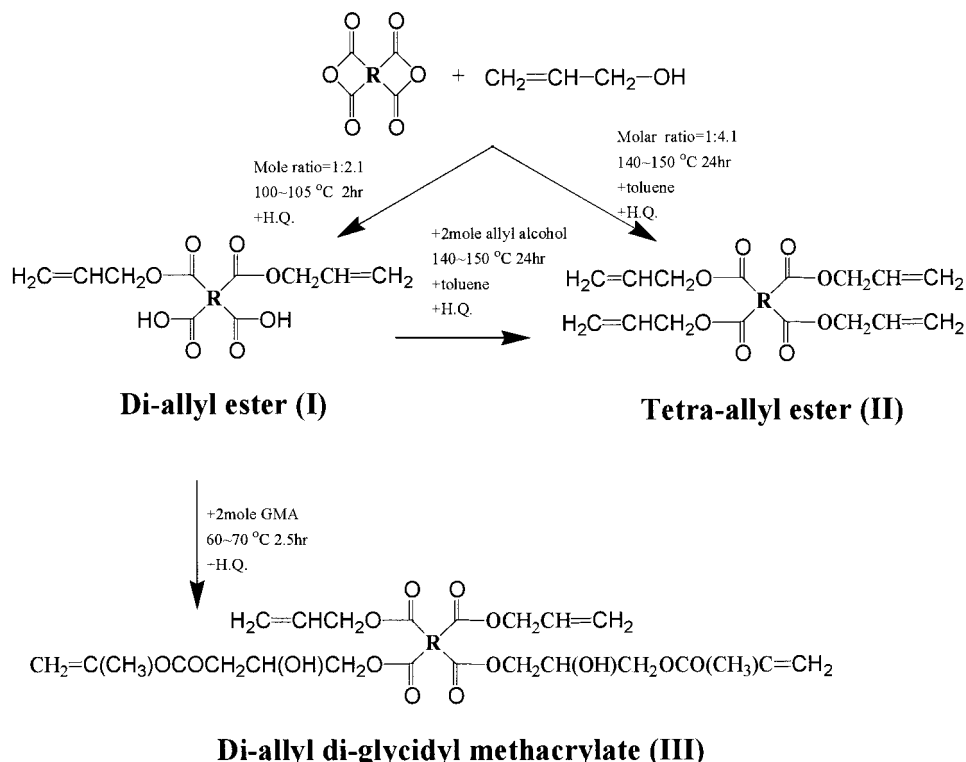
Synthetic procedure for the 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA)-based photocurable resins

UV-autocurable resins were synthesized as shown in Scheme 1. In the first step, in a suitable vessel equipped

Correspondence to: W.-Y. Chiang.

Contract grant sponsor: National Science Council of the Republic of China; contract grant number: NSC 89-2216-E036-009.

Synthesis Procedure



Scheme 1 Synthesis procedure.

with means for stirring and temperature control was mixed BTDA (32.2 g, 0.1 mol) with allyl alcohol (AAL; 13.9 g, 0.24 mol). The components were reacted at 100–105°C under a dry air atmosphere for 4 h and yielded benzophenone diallyl ester (I). The obtained mixture was poured by distillation and tested by IR. This reaction was confirmed by the disappearance of C=O and the stretching of the anhydride group at 1860 and 1790 cm^{-1} . After the reaction mixture cooled to 60°C, glycidyl methacrylate (GMA; 0.2 mol, 28.4 g) was added, and the temperature was maintained at 105–110°C for about 4 h; diallyl diglycidyl methacrylate (III) was obtained.

The diallyl ester with an excess of AAL and toluene was heated to 140°C in an open system vessel equipped with side and cooling tubes. Azeotropic distil-

lation (the azeotropic point was 78°C for water and benzene) was carried out to start esterification. The benzophenone tetraallyl ester (II) system was then obtained.

These two prepared resins could be irradiated directly or dithiol could be added to produce photocurable and addition reactions at the same time.

$^1\text{H-NMR}$ (δ , ppm) of III [see the H position (a–l) shown later in Fig. 3]: (a) 8.63, (b) 8.13, (c) 8.27, (d) 4.92, (e) 5.89, (f) 5.23, (g) 4.40, (h) 4.41, (j) 4.30, (k) 1.93, (l) 5.58

Synthetic procedure for the btda-based thio-ene system resins

In a suitable vessel equipped with a stirrer was mixed, at the proper temperature, the prepared ester (II or

TABLE I
Components and Properties of UV-Autocurable Esters (I and II)

Item	BA-12	BA-14	BAG-122	BAG-123	BAG-124
BTDA (mol)	1.0	1.0	1.0	1.0	1.0
AAL (mol)	2.2	4.2	2.2	2.2	2.2
GMA (mol)	0	0	2.0	3.0	4.0
Acid number	254	28.7	20.8	9.3	1.4
Doublebond content (%)	50	94.4	95.9	98.2	99.7
Color	All were transparent yellow.				
Solubility	Dissolved in acetone, chloroform, dioxane, THF, dimethylacetamide, dimethyl sulfoxide, dimethylformamide, <i>N</i> -methylpyrrolidone, and ethyl acetate. Insoluble in benzene, toluene, xylene, cyclohexane, methanol, ether, and hexane.				

III) with a dithiol compound [1,4-butanedithiol (BD) or 4,4'-thiol-bisbenzene-thiol (TBBT)] until the mixture was homogeneous. Some of the mixture was coated onto cleaned aluminum plates and flattened with the coating rod. The other part was placed between two Myler films, put in the book, and pressed with 20 kg of iron.

The prepared aluminum plates and Myler films were irradiated under a USH-500D high-pressure mercury lamp (wavelength = 500 nm; Ushio Electric Co., Tokyo, Japan) at a distance of 10 cm for various periods of time. The thickness of the members between the two Myler films was less than 1 mm, and the depth of the layers coated over the aluminum plates was 50 μm . The cured layers of the aluminum plates were used for tests of adhesion and chemical resistance. The cured membranes, after being peeled from Myler films and cut into small pieces (5 cm \times 0.5 cm), were used for tests of tensile properties.

Measurements of various properties

The characterization methods and curing process were performed according to previous studies.⁵ The double-bond content of the UV-autocurable resins was calculated from the acid number:

$$\text{Double-bond content} = (1 - A/A_0) \times 100\%$$

where A is the residual acid number and A_0 is the original acid number ($A_0 = 508 = 254 \times 2$, the number 254 being the acid value of BA-12).

RESULTS AND DISCUSSION

Characterization of the photocurable resins

Acid number and double-bond content

The acid value decreased from 303 mg of KOH/g to 254 mg of KOH/g, indicating that about 40% of the BTDA anhydride groups were open to the acid groups before the BTDA and AAL addition reaction occurred, as shown in Tables I and II. The acid numbers for BA-14 and benzophenone diallyl diglycidyl methacrylate ester (BAG-122) were 28.7 and 20.8, which indicates that the epoxy resin had a better degree of substitution than an alcohol-acid resin, resulting in the replacement of the group $-\text{COOH}$. We also used the acid number to calculate the double-bond content.

IR spectra analysis

This synthetic reaction was described in the previous sections. Scheme 1 summarizes these reactions. BTDA and AAL reacted at 105°C for 2 h and produced the diallyl ester (I). The IR spectrum of I is shown in Figure 1. The IR spectrum of the product mixture showed that the BTDA anhydride characteristic ab-

TABLE II
Components and Properties of UV-Autocurable Resins (I and II)

Item	BAGT-1221	BAGB'-1221	BAG-122	BAT-142	BAB'-142
BTDA (mol)	1.0	1.0	1.0	1.0	1.0
AAL (mol)	2.2	2.2	2.2	4.2	4.2
GMA (mol)	2.0	2.0	2.0	0	0
TBBT (mol)	2.0	0	0	2.0	0
BD (mol)	0	2.0	0	0	2.0
Color	(All are transparent brown yellow.)				
Solubility	Dissolved in acetone, chloroform, dioxane, THF, dimethylacetamide, dimethylsulfoxide, dimethylformamide, <i>N</i> -methylpyrrolidone, and ethyl acetate. Insoluble in benzene, toluene, xylene, cyclohexane, methanol, ether, and hexane.				

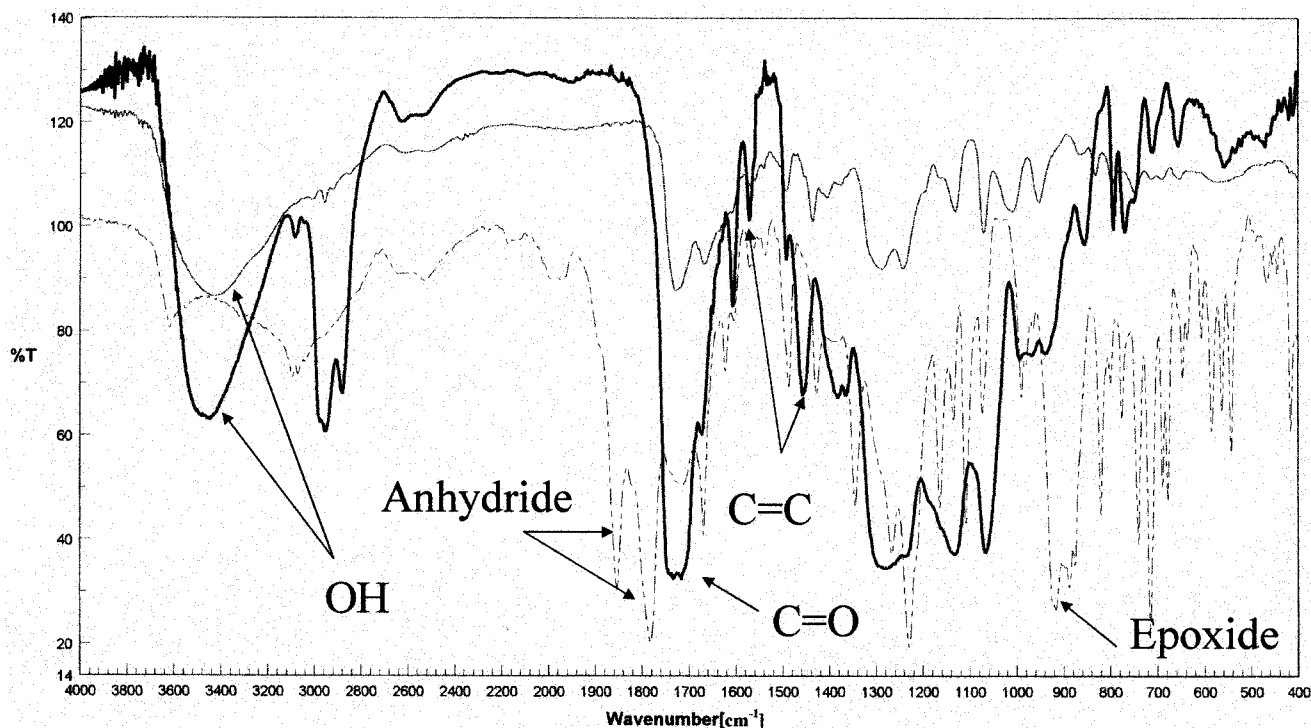


Figure 1 IR spectra of UV-autocurable resins (—), the half-ester intermediate BTDA-Allyl (---), and BTDA (· · ·).

sorption peaks at 1860 and 1790 cm^{-1} disappeared completely. The IR spectrum also showed the appearance of OH stretching at 3484 cm^{-1} due to the excess AAL monomer, C=C stretching at 1613 and 1474 cm^{-1} , C=O stretching of the ester group at 1726 cm^{-1} , and C=O stretching of the benzophenone (BP) group at 1668 cm^{-1} . The excess of the AAL monomer acted as a reactive diluent during the reaction. The IR spectrum showed that the epoxide group absorption peak at 910 cm^{-1} completely disappeared, and OH stretching appeared at 3484 cm^{-1} because of the ring-opening reaction of the epoxide and ester group. The spectrum showed a dithiol group absorption peak at 2550 cm^{-1} .

With the changing of the monomers, the mixture became *s*-BPDA- and PMDA-based. These reactions became the same procedure. Otherwise, the monomers *s*-BPDA and PMDA had the worse dissolution, so these esters were harder to obtain. This procedure required lots of AAL as a diluent. More than 4 mol of AAL was required in the reaction to produce the tetraallyl ester. The mixture was heated to 140°C to induce esterification, and toluene was added to produce an azeotrope. After 2 mol of water evaporated, the residual formed the desired ester (II). The BTDA-based esters were self-photocured because of the C=O structure. The *s*-BPDA-based and PMDA-based esters required BP as the photoinitiator. Otherwise, it was difficult for the mixture to reach a higher gel content. Figure 2 shows the IR spectra for the three kinds of tetraallyl esters.

II or III reacted with BD or TBBT to produce UV-curable resins via a thio-ene addition reaction that behaved similarly to the backbone thio-ene system method.

NMR spectra analysis

In the ^1H -NMR spectra of BAG-122, the Si-CH₃ group overlapped the internal standard tetramethylsilane at about 0–0.3 ppm. The GMA hydrogen of =C(CH₃)— (k) shifted to 1.9 ppm, —CH(OH)— (h, j) was around 4.3 and 1.9 ppm, —CH₂OCO— (i) and —OCOCH₂— (g) were around 4.5 ppm, and CH₂= (l) was around 6.14 and 5.50 ppm. The hydrogen of the allyl of CH₂= (f) was around 5.60 and 6.18 ppm, —CH= (e) was at 5.2 ppm, and —OCH₂— (d) was around 4.1 ppm. The phenyl group hydrogen =CH— (a–c) was at 8.6, 7.9, and 8.1 ppm, as shown in Figure 3.

Characterization of the cured membranes

Tensile properties

All BTDA-based cured membranes after extraction by tetrahydrofuran (THF) were cut into 5 cm × 0.5 cm pieces. The BAG-122 series membrane showed tough but brittle characteristics. It had a maximum breaking strength of 172.2 kg/cm² and an elongation of 6.8%. The BTDA-2Allyl-2GMA-TBBT (BAGT-1221) membrane showed worse breaking strength characteristics

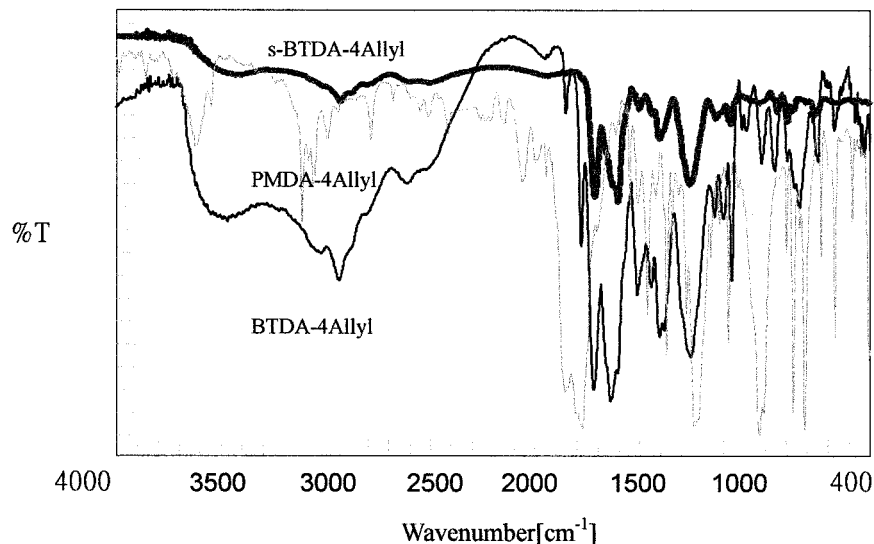


Figure 2 IR spectra of three kinds of tetraallyl esters.

than BAG-122 but better elongation characteristics. BAGT-1221 had the best breaking strength (168.7 kg/cm^2) of the four thio-ene resins, and the elongation was 11.3%. The BTDA-4Allyl-2TBBT (BAT-142) membrane had a breaking strength of only 128.4 kg/cm^2 , and its elongation was 15.2%. The BTDA-4Allyl-2BD (BAB'-142) membrane had the worst breaking strength (only 122.4 kg/cm^2), but the best elongation

(18.8%). With increasing allyl group content, the breaking strength decreased (BGH-122 had a breaking strength of 195.5 kg/cm^2 with zero allyl group content²⁵).

Table III shows two kinds of thio-ene resins. The breaking strength of the thio-ene-cured membranes increased with a decreasing dithiol reaction molar ratio. The elongation of the thio-ene-cured mem-

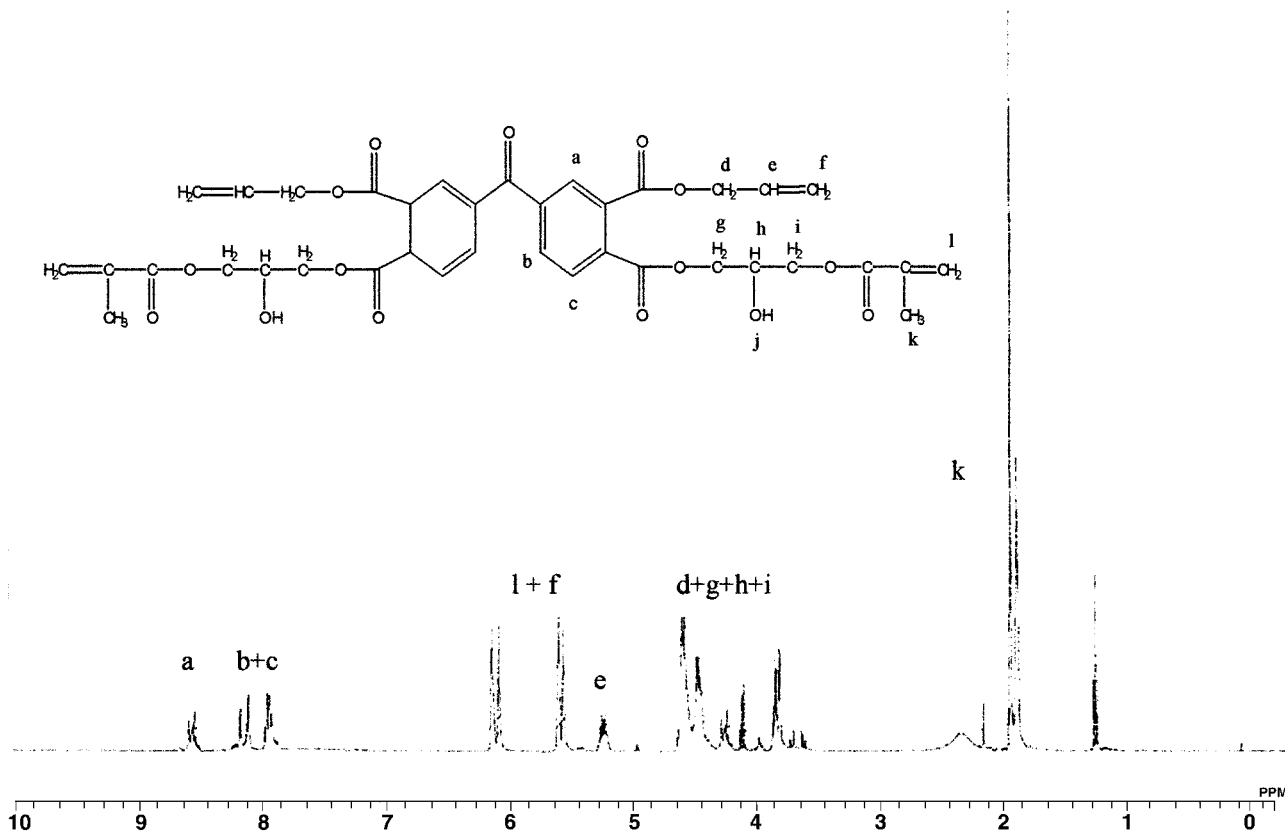


Figure 3 $^1\text{H-NMR}$ spectra of the UV-autocurable resin BAG-122.

TABLE III
Characteristics of the Different Ratios of the Thio-Ene Resins BAG-122 with TBBT/BD

Ratio (<i>m:n</i>)	<i>m</i> B-2A-2G + <i>n</i> T <i>n</i> B'							
	10:10		10:7		10:2		10:0 ^a	
Maximum gel content (%)	97	96	96	94	98	98	95	
Film formed	OK		OK		OK		OK	
Hardness	6 H		6 H		6 H		6 H	
Adhesion	100/100		100/100		100/100		100/100	
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		OK		OK	
Breaking strength (kg/cm ²)	168.7	156.6	170.4	162.4	171.7	170.4	172.2	
Elongation (%)	11.3	14.8	8.4	10.4	7.4	7.3	6.8	

B = BTDA; A = AAL; G = GMA; T = TBBT; B' = BD.
^a 10:0 means BAG-122.

branes increased with an increasing dithiol reaction molar ratio.

Table IV shows a comparison of the breaking strength and elongation for all the resins. The breaking strength test results showed BAG-122 > BAGT-1221 > BAGB'-1221 > BAT-142 > BAB'-142. The elongation results showed BAB'-142 > BAT-142 > BAGB'-1221 > BAGT-1221. (where BAGB'-1221 is BTDA-2Allyl-2GMA-BD).

Thermal properties

A DSC analysis of BAG-122-cured resins is shown in Figure 4. DSC for BAG-122 showed a glass-transition temperature (*T_g*) of 166.6°C (lit.⁵ -10 to 60°C).

Coating properties

A comparison of the gel contents of different kinds of resins is shown in Figure 5. BAT-142 (*N* = 4) required the longest irradiation time, and the gel content reached only 90% after 14 min of irradiation. The effect of irradiation on the resins in different atmospheres is shown in Figure 6. Oxygen had little effect on BAG-122 because its two lines were close enough to ignore. The performance values of the prepared esters coated onto the aluminum plates are shown in Table IV. The cured coating for BAG-122 and BAGT-1221 showed excellent results. The hardness characteristics of the prepared esters that showed no groups or diallyl groups (*N* = 0 or 2) reached 6H within 1 h of irradiation.

TABLE IV
Overall Comparison of the Number of Allyl Group Resins

	BAT-142	BAB'-142	BAGT-1221	BAGB'-1221	BAG-122	BGH-122 ^a	BGM-122 ^a
Number of allyl groups (<i>N</i>)	4	4	2	2	2	0	0
Gel content (%)	88	90	97	96	95	96	92
Film formed	OK						
Hardness	< 6 H	< 6 H	6 H	6 H	6 H	> 4 H	> 4 H
Adhesion	100/100	100/100	100/100	100/100	100/100	100/100	100/100
Acid corrosion test (5% HCl, 72 h)	OK						
3% Acetic acid, (72 h)	OK						
Salt corrosion test (5% NaCl, 72 h)	OK						
Alkali corrosion test (1% NaOH, 72 h)	OK						
Breaking strength (kg/cm ²)	128.4	122.2	168.7	156.3	172.2	195.5	166.5
Breaking strength (MPa)	12.6	12.0	16.5	15.3	16.9	19.2	16.3
Average Elongation (%)	15.2	18.8	11.3	14.8	6.8	4.4	4.9

A = AAL; G = GMA; T = TBBT; B' = BD; H = 2-hydroxyethyl acrylate; M = 2-hydroxyethyl methacrylate.
^a Ref. 26.

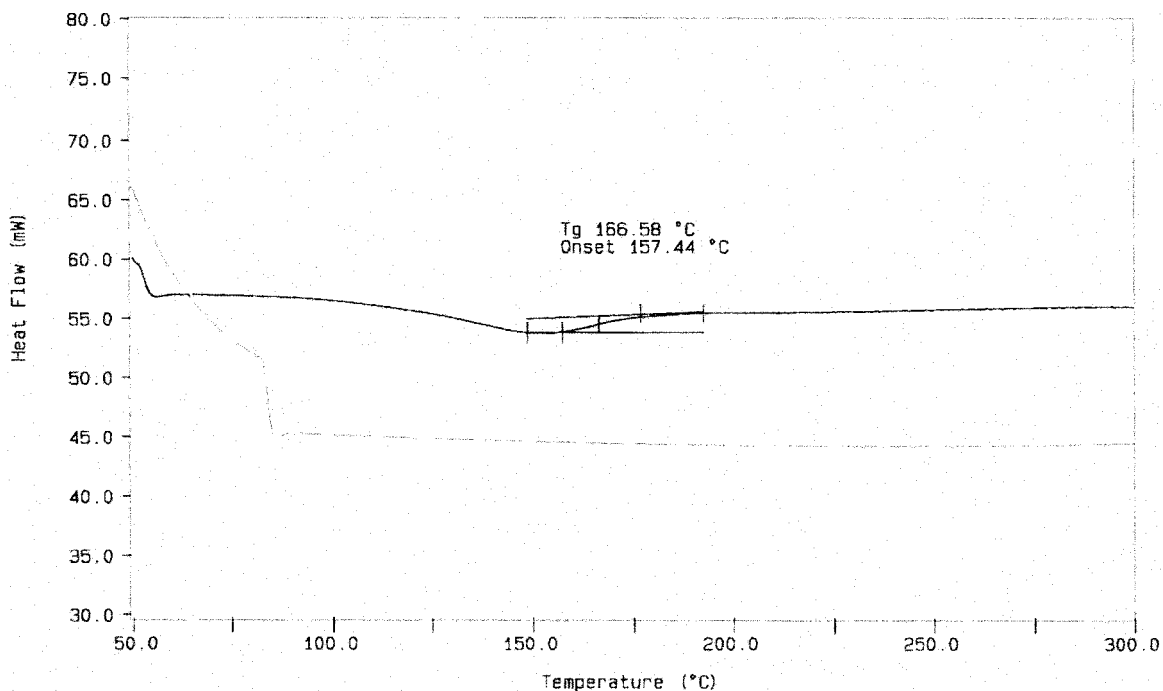


Figure 4 DSC spectra of the photocurable resin BAG-122.

ation, with a gel content greater than 95%. The hardness of the resins that had tetraallyl groups ($N = 4$) did not reach 6H, and the gel content did not reach 95% after 1 h of irradiation. This occurred because of the lack of acrylic groups, and only an addition reaction occurred. All coated plates showed good resistance in the acid, salt, and alkali corrosion tests.

CONCLUSIONS

The UV-autocurable BTDA-based multifunctional esters containing the allyl group were successfully synthesized. The *s*-BPDA- and PMDA-based esters failed to form membranes because of their poor solubility.

The BTDA-based multifunctional esters containing the allyl group not only had traditional photocurable agents and kept the advantages of acrylate resins but also behaved like added thio-ene, which could react with dithiol compounds. T_g 's of these cured resins ranged from 163 to 169°C, as determined by DSC. The prepared membranes exhibited strengths at break-points of 144–172 kg/cm², and the membrane hardness reached 6H. The average elongations were about 9%. The cured coating also showed excellent resistances to acid, alkali, and salt corrosion. In the $N = 2$ series (two allyl groups and two acrylic groups), the BAG-122-cured resin had the highest Young's modulus and breaking strength. The BAGT-1221-cured resin

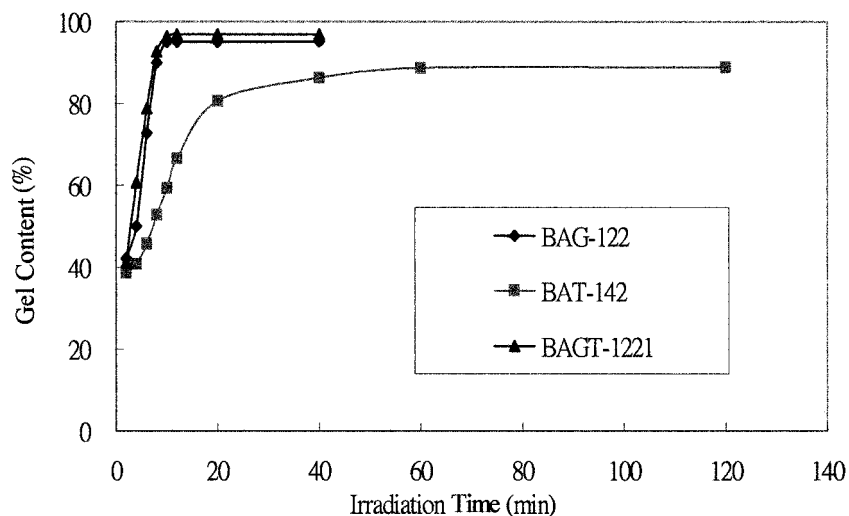


Figure 5 Comparison of the gel contents of different kinds of resins.

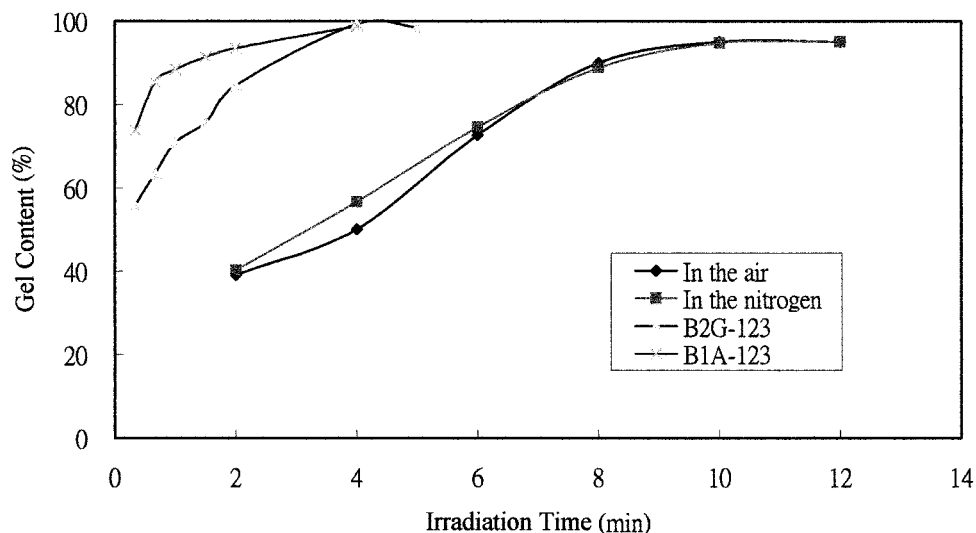


Figure 6 Effect of the irradiated resins in different atmospheres.

had the highest elongation, possibly produced by dithiol. In the $N = 4$ series (four allyl groups), the BAT-142-cured resin had the highest Young's modulus and breaking strength. The BAB'-142-cured resin had the highest elongation. With increased curing time, the reduced oxygen affected the photocurable resins. The breaking strength of the thio-ene-cured membranes increased with a decreasing dithiol reaction molar ratio. The breaking strength and Young's modulus results were BAG-122 > BAGT-1221 > BAGB'-1221 > BAT-142 > BAB'-142. The elongation results were BAB'-142 > BAT-142 > BAGB'-1221 > BAGT-1221.

The authors express their gratitude to Dr. T. S. Lin, the president of Tatung University, for his kindness and encouragement. They give special thanks to Dr. Vincent Chuang, the former president of Union Carbide Formosa Co., Ltd., for his valuable suggestions during the course of this study.

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