

Preparation and Properties of UV-Autocurable BTDA-Based Polyurethane Methacrylates

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Synopsis

Syntheses of several UV-autocurable methacrylourethanes and the effects of polyol type on their properties are investigated. Autocurable benzophenone tetracarboxylic dianhydride (BTDA)-based polyurethane methacrylates are prepared by addition reaction from benzophenone tetracarboxylic dianhydride (BTDA), 2,4-toluene diisocyanate (TDI), 2-hydroxyethyl methacrylate (HEMA), and polyol (polyethylene glycol, polydiethylene succinate, polydiethylene maleate, or polydiethylene hexamethylene-dicarbamate). Autocurable oligomers possess good pot life and are cured rapidly when exposed to ultraviolet (UV) radiation without the addition of photoinitiator. The different polyols are used to obtain wide range properties of cured films with a glass transition temperature (T_g) range of -10.5 – 5.5°C . Increasing the T_g of polyol shifts the dynamic mechanical storage modulus and loss factor of the cured film to high temperature. For practical application, oligomer is mixed with reactive monomers to bring the systems to a workable viscosity at room temperature. Among the monomers, the higher the composition of hydroxyethyl acrylate in the oligomer-monomer system, the higher the curing rate of the system as compared with neat oligomer. Moreover, increasing the chain length of dimethacrylate monomers results in a decrease in breaking strength from 160 to 140 kg/cm², in Young's modulus from 771 to 400 kg/cm², and in glass transition temperature from 18 to 6.5°C, while the elongation at breaking increases from 70 to 130%.

INTRODUCTION

Since the development of high intensive radiation processing, such as ultraviolet light and electron beams,^{1,2} as an alternative to heat processing, photocurable resins are now widely used for coating, printing, adhesion, and photoimaging.³⁻⁶ In general, photocurable resins consist primarily of monomers and oligomers with acryl^{7,8} or methacryl⁹⁻¹³ double bonds. For fast and efficient curing of such resins, it is necessary to include a relatively large amount of the initiating component within the system. However, such levels of photoinitiator cannot be used in certain systems in which high levels of photoinitiator will not dissolve or mix homogeneously.

Many solid initiators^{14,15} used as photoinitiators may present disadvantages in terms of uniform dispersion, volatility, and migration of initiating materials. Many patents related to oligomers having built-in photoinitiators, which are autopolymerizable through ultraviolet (UV) radiation, have been reported.¹⁶⁻¹⁸

For the above reasons, this article describes the syntheses of a series of autocurable polyurethane methacrylates having different polyol structures of

comparable molecular weight. The effects of various polyols on the curing rate and storage ability, as well as tensile properties, are discussed in detail. The rheological and thermal properties of such autocurable resins after curing are also investigated. Furthermore, the effects of various added reactive monomers¹⁹⁻²⁷ on the properties of cured films are reported.

EXPERIMENTAL

Materials

Diethylene glycol (DEG), maleic anhydride (MA), and succinic anhydride (SA) used in synthesizing oligoesters were reagent grade and used without further purification. 1,6-Hexamethylene diisocyanate (HDI), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 2,4-toluene diisocyanate (TDI), and 2-hydroxyethyl methacrylate (HEMA) were extra pure grade from Tokyo Kasei, Japan. Polyethylene glycol (PEG) was reagent grade from Wako Pure Chemical Industries Ltd., Japan; the number average molecular weight \bar{M}_n was about 400. Solvents, tetrahydrofuran (THF), and methanol (MeOH), were distilled before use.

Syntheses

Polydiethylene Maleate (UES) and Polydiethylene Succinate (SES).

A four-necked flask was equipped with a magnetic stirrer, condenser, thermometer, and nitrogen inlet. In the flask was placed diethylene glycol and anhydride (maleic anhydride or succinic anhydride) with a molar ratio of glycol and anhydride at 2.3:1. The mixture was heated at 120°C for 3 h and then at 190–200°C for another 15 h. Water formed from the condensation reaction was continuously distilled from the reactor. When the acid number reached below 5, the mixture was distilled to remove the unreacted materials under reduced pressure. The resulting polydiethylene maleate, designated UES for unsaturated oligoester, was a slightly yellowish transparent viscous liquid, with a molecular weight of about 472 determined by end-group titration analysis (acid number, 3.6 and hydroxyl number, 230.5). The polyethylene succinate, designated SES for saturated oligoester, was a colorless transparent viscous liquid, with a molecular weight of about 427 (acid number, 3.85 and hydroxyl number, 255). The molecular weight was calculated from the following equation:

$$\text{corrected hydroxyl No.} = \text{acid No.} + \text{hydroxyl No.}$$

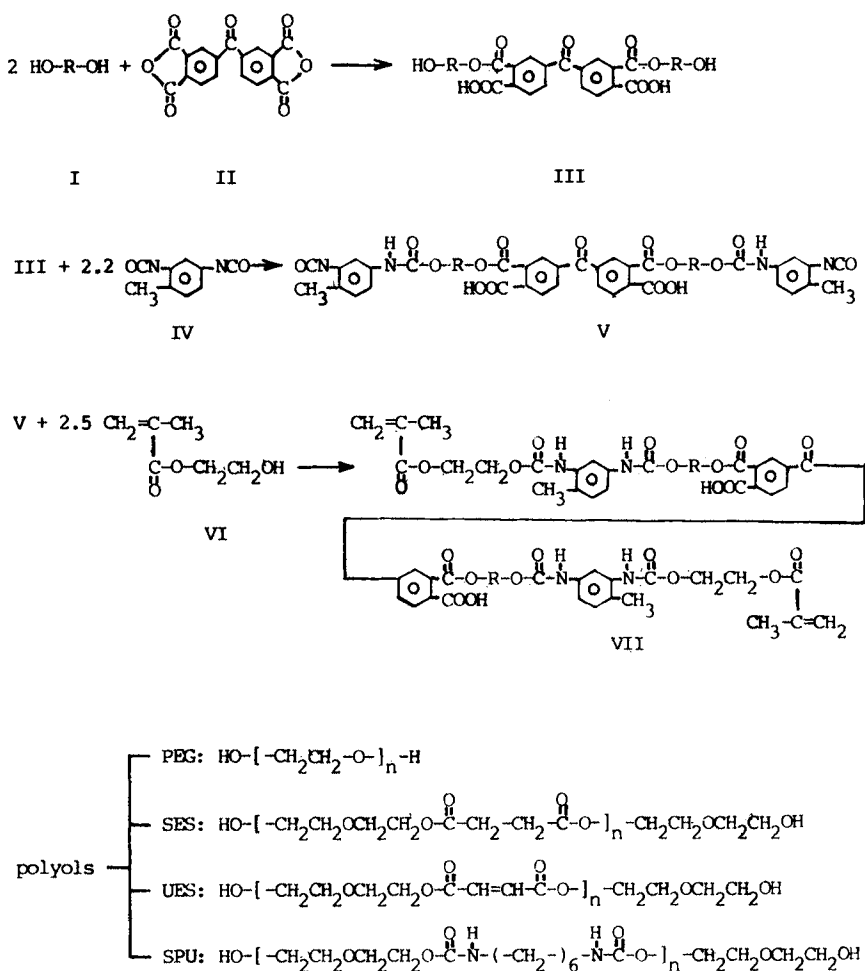
$$\text{Molecular weight} = \frac{2 \times 56.1 \times 1000}{\text{acid No.} + \text{corrected hydroxyl No.}}$$

Polydiethylene Hexamethylenedicarbamate (SPU). A four-necked flask was equipped with a magnetic stirrer, condenser, thermometer, pressure-equalizing dropping, and nitrogen inlet. The flask charged with diethylene glycol was heated to 90°C, and hexamethylene diisocyanate was added dropwise with the molar ratio of glycol and diisocyanate at 2.4:1. When the

addition was completed, the mixture was heated at 120°C for 2 h. The product was purified by washing three times with anhydrous methanol and drying under vacuum. The resulting polydiethylene hexamethylenedicarbamate, designated SPU for saturated polyurethane, was a white solid at room temperature, and the yield was about 84%.

BTDA-Based Polyurethane Methacrylates. 2-Hydroxyethyl methacrylate (HEMA)-capped polyurethane-methacrylate oligomers based on BTDA (VII; UM-PEG, UM-SES, UM-UES and UM-SPU) were synthesized according to Scheme I.

In the first step, 0.3 mol of polyol (I: 120 g of PEG, 128.1 g of SES, 141.6 g of UES, or 114.1 of SPU) was reacted with 0.15 mol of benzophenone



Scheme I. Syntheses of autocurable polyurethane methacrylates: I. Polyols: polyethylene glycol (PEG), polydiethylene succinate (SES), polydiethylene maleate (UES) and polydiethylene hexamethylenedicarbamate (SPU). II. BTDA. III. Half ester adduct of polyols and BTDA. IV. 2,4-Toluene diisocyanate. V. Isocyanate-capped intermediate. VI. 2-Hydroxyethyl methacrylate. VII. Autocurable oligomers (UM-PEG, UM-SES, UM-UES and UM-SPU four types).

tetracarboxylic dianhydride (II, 48.3 g) under nitrogen atmosphere for 2 h at 100°C and for another 1 h at 120°C. The mixture, a transparent viscous liquid, was cooled to room temperature. In the second step, the half-ester adduct of polyol and BTDA (III) was reacted with 0.33 mol of 2,4-toluene diisocyanate (IV, 57.5 g) in THF (100 mL) under nitrogen with stannous octoate as catalyst. The solution was successively stirred for 3 h at 40°C and then heated to 60°C to force the reaction to completion. In the third step, the isocyanate-capped intermediate (V) was reacted with 0.38 mol of HEMA (VI, 49.5 g) in the presence of hydroquinone under air for 5 h at 65°C. Each reaction was undertaken in the same flask as the first step without isolation. The completion of the reaction were confirmed by the disappearance of the peak caused by $\text{N}=\text{C}=\text{O}$ stretching absorption near 2280 cm^{-1} by infrared (IR) spectroscopy.

MEASUREMENT OF VARIOUS PROPERTIES

IR Spectra

Infrared spectra of oligomers were obtained on a JASCO Model A-202 spectrophotometer.

Photocuring

Prepared oligomers were cast between two Mylar films and irradiated by a high-pressure mercury lamp (Model USH-500D manufactured by Ushio Electric Co., Japan), at a distance of 30 cm for various lengths of time.

Pot Life

Oligomers were put into an aging oven for a week at various temperatures, and then extracted by THF to determine their gel content.

Gel Content

Oligomers after photocuring or thermocuring were extracted by THF at 60°C for 12 h and residual polymers were dried and weighed.

Molecular Weight

Oligomers (0.5 wt%) in THF solution were injected 10 μL into a Shimadzu Liquid Chromatography Model LC-5A that was equipped with an UV detector (Model SPD-2A, wavelength 254 nm, range 128) and RI detector (Toyo Soda, Model RI-8000, range 256). The columns used were TSK-G1000HXL, TSK-G2000HXL and TSK-G3000HXL, at room temperature with a flow rate of 1 mL/min and pressure below 50 kg/cm². The calibration curve was plotted by using monodisperse polystyrene and hydroquinone.

Viscosity

The viscosity of oligomers was measured at 40°C using a Brookfield Viscometer Model LVF.

UV Absorption Spectra

Ultraviolet (UV) absorption spectra of oligomers in dioxane solution were obtained using a Varian UV-Vis Spectrophotometer Model DMS-90. All measurements were carried out in 1-cm quartz cell, scanned from 400-200 nm.

Tensile Properties

Cured films were cut into 50×6 mm strips. After conditioning for 24 h at room temperature, the specimen was clamped in an Instron Testing Machine, Model 1130, with a jaw separation of 2 cm and extended at a rate of 5 cm/min to failure. The tensile strength, Young's modulus, and elongation at break were determined from the load extension diagram.

Thermal Properties

Thermogravimetric analysis (TGA) was carried out on a Du Pont 951 Thermogravimetric Analyzer using nitrogen as the carrier gas. About 10 mg of each sample was heated with a rate of $20^\circ\text{C}/\text{min}$ over a temperature range of $100\text{--}560^\circ\text{C}$.

Thermomechanical analysis (TMA) of the glass transition temperature (T_g) was performed on a 943 Thermomechanical Analyzer, Du Pont Instruments 1090B Analyzer, using a penetration probe with a load of 2 g at a heating rate of $2^\circ\text{C}/\text{min}$. The sample at a thickness of about 0.2 mm was measured in a temperature range of $-50\text{--}60^\circ\text{C}$.

Dynamic mechanical analysis (DMA) was run in the resonant model at 2–20 Hz from the Du Pont 9900 data station connected to 983 Dynamic Mechanic Analyzer. Cured films of about $8 \times 0.25 \times 5.5$ mm were tested with a horizontal clamp from -130 to 70°C at a heating rate of $5^\circ\text{C}/\text{min}$ and amplitude of 0.2 mm.

RESULTS AND DISCUSSION

IR Spectra of Autocurable Resins

The IR spectra of BTDA-based polyurethane methacrylate (UM-PEG) and its related intermediates are given in Figure 1. Half-ester adduct of BTDA (III) gave an ester absorption peak at 1740 cm^{-1} , and OH hydroxy group at 3400 cm^{-1} , but the anhydride characteristic absorption peak of the BTDA at 1860 cm^{-1} completely disappeared. The half-ester adduct (III) was reacted with *para*-NCO group of 2,4-TDI, which still retained an *ortho*-NCO absorption peak at 2280 cm^{-1} , while the hydroxy group of half-ester (III) at 3400 cm^{-1} was converted to a sharp NH absorption peak of urethane of isocyanate-capped intermediate at 3350 cm^{-1} . The absorption peak of NCO gradually decreased during the reaction of isocyanate intermediate with HEMA. After another 5 h of reaction time, the peak at 2280 cm^{-1} disappeared, indicating the reaction was completed. The IR spectra of four types of autocurable resins (UM-PEG, UM-SES, UM-UES, and UM-SPU) based on different polyols at comparable molecular weight showed the same characteristic absorption peak in Figure 2, due to similar functional groups in their structure.

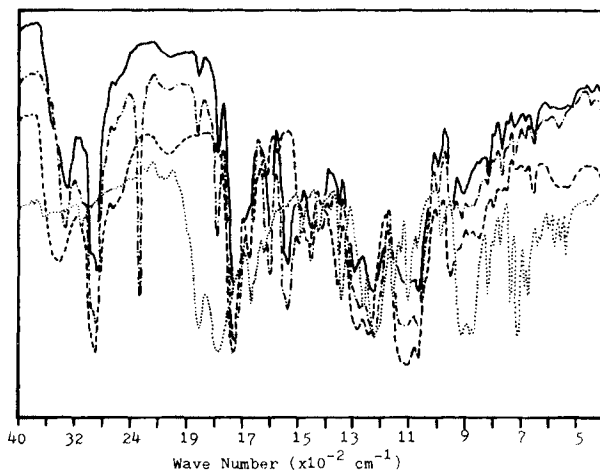


Fig. 1. IR spectra of BTDA (·····), half ester of BTDA and PEG (-----), isocyanate-capped intermediate (-·-·-·), autocurable oligomer (UM-PEG, —).

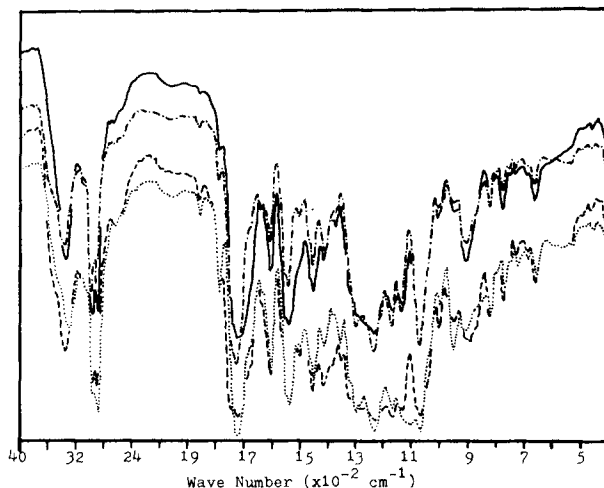


Fig. 2. IR spectra of autocurable oligomers: (·····) UM-PEG; (-----) UM-SES, (-·-·-·) UM-UES; (—) UM-SPU.

UV Absorption Spectra of Autocurable Resins

DePoortere and co-workers,²⁸ asserted that the rate of photoinitiated polymerization is a function of the square root of benzophenone concentration, which magnifies the effect of low photoinitiator concentration. Figure 3 shows the UV absorption of resins which increases with increasing wt% of BTDA in the autocurable resin and maintains the following order: UM-SPU > UM-PEG > UM-SES > UM-UES. Therefore, we predicted that the rate of photoinitiated polymerization of resins might follow the same tendency.

Fundamental Properties of Autocurable Resins

The fundamental properties such as the number-average molecular weight obtained from GPC, viscosities, pH, and solubilities of prepared oligomers are

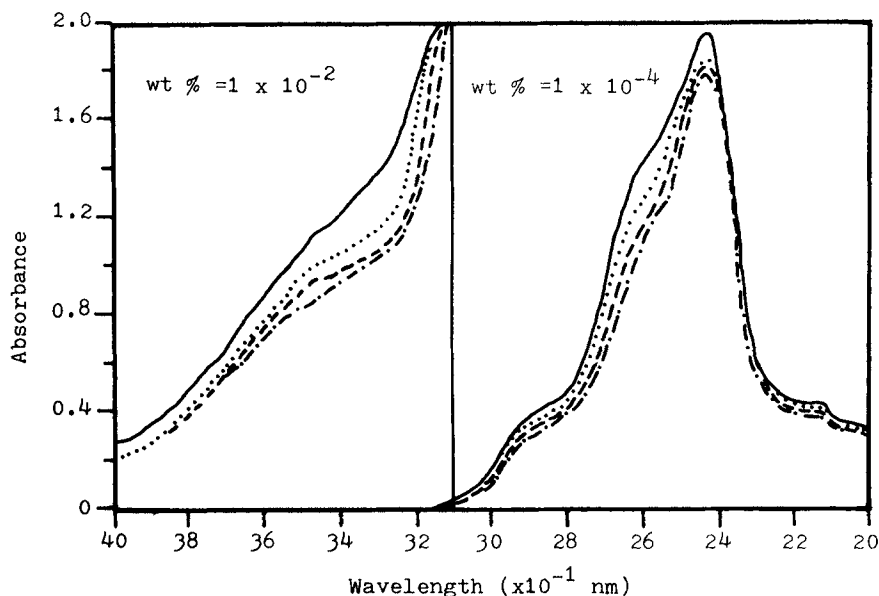


Fig. 3. UV absorption spectra of oligomers: (.....) UM-PEG; (-----) UM-SES; (-·-·-) UM-UES; (—) UM-SPU.

TABLE I
Properties of BTDA-based Polyurethane Methacrylates

Properties	UM-PEG	UM-SES	UM-UES	UM-SPU
\bar{M}_n	2060	2470	2610	2210
Viscosity (cP)	23250	25700	28100	35500
pH Value	4.5	5.0	5.8	4.5
Solubility	(Dissolves in acetone, chloroform, dioxane, THF; insoluble in BTX, alcohols, cyclohexane, and CCl_4)			
Color	(All are transparent yellowish-brown)			
Wt% of unreacted HEMA ^a	4.5	2.7	2.5	5.2

^aWt % of unreacted HEMA in resin is measured from the GPC chromatogram. Abbreviation: BTX = benzene, toluene, and xylene.

listed in Table I. In coating and printing applications, the viscosity of solvent-free oligomers is of primary concern. The data in Table I show that the viscosity of oligomers increases with increasing number-molecular weight of oligomers, except for the UM-SPU oligomer. The high bulk viscosity of UM-SPU oligomer is attributed to the fact that this oligomer is more polar than the others.

Pot Life and Curing Rate of Autocurable Resins

Autocurable resins must be activated by radiation, such as ultraviolet light, electron beam, and gamma radiation. At the same time they also must be inactive at ambient temperatures for storage and handling stability. To evaluate their properties, autocurable resins were baked in an aging oven at 120–180°C using four different temperatures for a week. From Table II we see

TABLE II
Pot Life and Photocuring Rate of BTDA-based Polyurethane Methacrylates

Gel content, %	Baking temperature (°C)				Irradiation time (s)					
	120	140	160	180	1	3	10	20	30	40
UM-PEG	0	0	63.5	77.4	70	80	83	84.5	84.7	86.5
UM-SES	0	0	82	98	64.7	68.8	71	74	75	75.5
UM-UES	0	81	90	99	60	63	64.5	65	67	70
UM-SPU	0	0	50	70	64.7	70.6	72	78	80	81

that all the resins possess good pot life below 140°C without gelation. The UM-UES oligomer has the poorest thermal stability due to the presence of an unsaturated group in the polyol segment. All autocurable resins were very sensitive to sunlight in the absence of air. Their gel contents ranged from 46 to 90% after irradiation of 2 min in sunlight.

The autocurable resins were cured directly by UV without the addition of any photoinitiators. The curing process was carried through a transparent Mylar film to prevent the influence of oxygen. If the covering film were removed immediately after 3 s of irradiation, the resin remained sticky, and the gel content was below 80%. However, if the film was removed 2 h after the irradiation (this process is defined as postcuring), the surface of the cured resin was hard and smooth, and its gel content was greater than 90%. These autocurable resins were found to be better than photocurable resins that were prepared using benzoin ethyl ether as the initiator in terms of gel content and curing rates.^{9,10}

In order to determine the curing rates of several autocurable oligomers, the gel content of cured films was determined immediately after irradiation without passing the postcuring process. The results are listed in Table II. All oligomers are cured rapidly with 1 s and then leveled off in 6 s. The curing rate of resins shows the following order: UM-PEG > UM-SPU > UM-SES > UM-UES. Except UM-SPU, this tendency coincides with the UV absorption of oligomers. The low curing rate of UM-SPU is attributed to the fact that the prepared oligomer contains too much unreacted HEMA (the curing rate affected by HEMA monomer will be presented in oligomer-monomer system). Therefore, the curing rate of autocurable oligomer seems to depend on the wt% of BTDA and the residual wt% of unreacted HEMA in the oligomer.

Effect of Irradiation Time and Polyol Type on Properties of Cured Oligomers

Table III shows that mechanical properties such as tensile strength and Young's modulus at break increase while elongation at break decreases as the irradiation time increases. These properties tend to level off when the irradiation time exceeds 10 s. This is because the properties are related to the crosslinking density, which nearly reaches the maximum with 10 s of irradiation. Beyond that time, migration of initiating material is limited; therefore, the crosslinking density increases slowly. There exists a critical point at an irradiation time of 6 s for elongation at break. During the first 6 s exposure

TABLE III
UV Irradiation Time on Tensile Properties of Oligomer Type UM-PEG
after Postcuring Process

Irradiation time (s)	1	3	10	20	30	40
Gel content (%)	80.2	89.3	90	90.3	91	91.7
Young's modulus (kg/cm ²)	66.6	78	76	76	81.6	80
Breaking strength (kg/cm ²)	40.4	47.7	51	54.8	59.2	64.7
Elongation (%)	116.5	162.3	148	136	130.5	128

TABLE IV
Tensile and Other Properties of Cured Oligomers at Comparable Gel Content

Type of oligomer	UM-PEG	UM-SES	UM-UES	UM-SPU
Gel content (%)	91.7	94.0	90.4	90.0
Pencil hardness ^a	B	HB	2H	H
T_g of cured film (°C)	-10.5	-0.5	4	5.5
Young's modulus (kg/cm ²)	80	282	320	335
Breaking strength (kg/cm ²)	64.7	80	102	108
Elongation at break (%)	128	110	96.3	165

^a Pencil hardness is determined as a measure of surface hardness according to JIS K 5651.

time, the crosslinking density was not sufficient to toughen the cured film; this resulted in a lower elongation at break.

To eliminate the effect of crosslinking density, the gel content of cured oligomers was fixed at nearly 91%. The effect of the type of polyol of comparable molecular weight on tensile properties, pencil hardness, and glass transition temperature (T_g) of cured films were determined and listed in Table IV. The T_g was determined from the onset of TMA curves. The polydiethylene hexamethylenedicarbamate (SPU)-based autocurable oligomer has the highest T_g followed by polydiethylene maleate (UES) and polydiethylene succinate (SES)-based oligomers; the polyethylene glycol (PEG)-based sample having the lowest T_g . This trend is consistent with the chain flexibility of the various polyols.

The tensile properties of cured oligomers are also affected by polyol structure; for example, the SPU-based sample exhibit strong and tough properties with the highest breaking strength, Young's modulus, and elongation at break. The trend of Young's modulus and breaking strength are in agreement with that of glass transition temperature for cured films, because decreasing T_g of cured films leads to a more flexible molecular chain and reduces the Young's modulus and breaking strength.

Effect of Polyol Type on Thermal Properties

The thermal stability of cured films will be a function of the structure of polyols. The TGA analysis of autocurable resins is shown in Figure 4; thermal stability follows the tendency: PEG > UES > SES > SPU-based materials. All the cured films possess good thermal stability, and the major decomposition temperatures are all above 290°C.

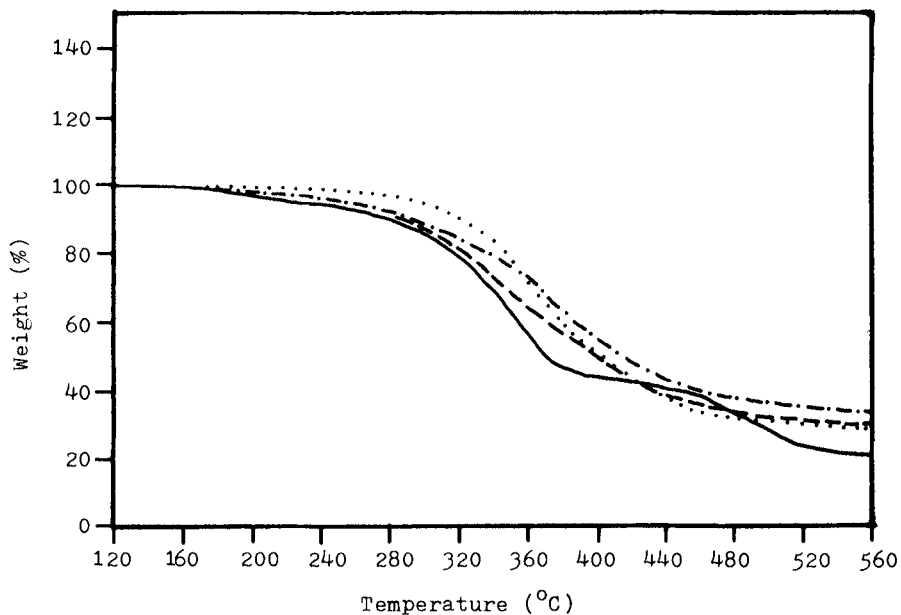


Fig. 4. Thermal decomposition analysis of autocurable oligomers: (.....) UM-PEG; (-----) UM-SES; (-·-·-·) UM-UES; (—) UM-SPU.

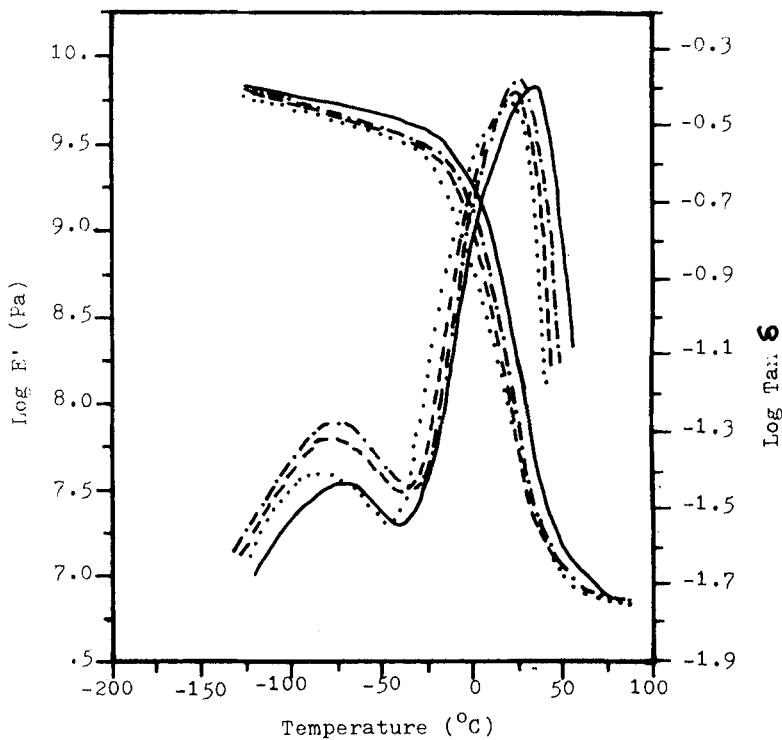


Fig. 5. Dynamic mechanical storage modulus and loss factor curves of cured oligomers: (.....) UM-PES; (-----) UM-SES; (-·-·-·) UM-UES; (—) UM-SPU.

The dynamic mechanic storage modulus (E') and loss factor ($\tan \delta$) curves for the cured films are shown in Figure 5. The loss factor curves exhibit peaks at approximately -77 and 26°C . The peaks at -77°C are attributed to T_g of the polyol segment, which show the following order: SPU > UES > SES > PEG. The other peaks show the development of urethane methacrylate phase,²⁹ and shift to higher temperature with increasing the T_g of the polyol segment. The storage modulus curves show differences in the transition region, and the positions of transition temperature range from -14 to 0.5°C . The increase of the storage modulus in the transition region is primarily due to an increasing polyol T_g which shifts the storage modulus to higher temperature. The transition temperature trend of cured film with polyol types (SPU > UES > SES > PEG-based sample) parallels the T_g noted in the TMA curves.

Curing Rate of Oligomer-Monomer Systems

As expected, the addition of monomers reduced the viscosity substantially and made it possible to cast the films easily at room temperature. Furthermore, the UM-SPU oligomer had the best curing rate, strength, and toughness properties of cured film among the oligomers.

To reduce the influence of oxygen, the mixtures of oligomer and monomers were directly cured by UV through transparent Mylar film without the addition of photoinitiator. The curing rates of monofunctional and difunctional monomer-oligomer systems, consisting of 20% monomer and 80% oligomer by weight, are listed in Table V. The response of these systems to UV radiation is different from the neat oligomers. Monomers such as HEMA, GMA, EGDMA, and DEGDMA showed less response, which was attributed to diluting the content of benzophenone moiety in systems. However, systems containing monofunctional HEA and AMA, as well as difunctional TiEGDMA and TeEGDMA, had the higher response. Although the exact reason for the effect of these monomers on the curing rate of these systems is not quite clear,

TABLE V
Effect of Reactive Monomers on the Percent Gel of Oligomer-Monomer Systems.
Oligomer/Monomer = 80/20 by weight.

Gel content, %	Irradiation time (s)				
	3	6	10	20	30
HEMA	10	20	46.9	88.7	89
HEA	77	80	81	87.7	90
GMA	6.5	16	31.8	85	87.7
AMA	67	76	82.2	87.7	90.1
EGDMA	16	37	64.2	84.5	87.7
DEGDMA	34.8	61	78.4	88	91
TiEGDMA	42.9	68	82	88	90.5
TeEGDMA	62.5	76	84	90	91

HEMA = hydroxyethyl methacrylate; HEA = hydroxyethyl acrylate; GMA = glycidyl methacrylate; AMA = dimethylaminoethyl methacrylate; EGDMA = ethylene glycol dimethacrylate; DEGDMA = diethylene glycol dimethacrylate; TiEGDMA = triethylene glycol dimethacrylate; TeEGDMA = tetraethylene glycol dimethacrylate.

the higher response of HEA system as compared to pure oligomer might be explained by the higher UV curing rate of acrylates than methacrylates. The increased curing rate of the AMA system might be attributed to the abstraction of hydrogen by the benzophenone moiety on the oligomer from AMA and formation of a radical that initiates polymerization. In difunctional monomer cases, the curing rate of systems increased with increasing the chain length between two methacrylate groups, and maintained the following order: TeEGDMA > TiEGDMA > DEGDMA > EGDMA.

Effect of Monomers on Properties of Cured Films

Tensile properties and glass transition temperature of films made from 80 wt% oligomer and 20 wt% monomer and cured at irradiation time of 30 s are listed in Table VI. Except for GMA monomer, systems containing mono-monomers decreased the breaking strength, Young's modulus, and T_g of cured films, while increasing the percentage elongation as compared to the neat oligomer. However, difunctional monomers exhibit the opposite response because the properties of films are related to the crosslinking density, which increases for systems containing difunctional monomers, and decreases for systems with monofunctional monomers. Moreover, increasing the chain length between the two methacrylate groups of dimethacrylate monomers resulted in decreased breaking strength, Young's modulus, and T_g while elongation at break increased.

The tensile properties and T_g of cured films are also affected by chain stiffness or flexibility of the monomers. The system containing GMA monomer raises the breaking strength, Young's modulus, and T_g of the film while lowering the elongation at break as compared to pure oligomer. This phenomenon is attributed to a large and rigid epoxy group in the GMA monomer. The Young's modulus of cured films for mono-monomer systems maintained the following order: GMA > AMA > HEMA > HEA. Finally, the tensile properties of HEA and HEMA systems were almost in the same quantities because of their mutual hydroxy end group.

The effect of the monomer 5% to 30% monomer concentration on tensile properties and T_g are shown in Table VII. The results show that the greater

TABLE VI
Effect of Monomers on Tensile Properties of Cured Films in
Oligomer-Monomer Systems (Oligomer/Monomer = 80/20 by Weight)

Monomer	F	YM (kg/cm ²)	TS (kg/cm ²)	E (%)	T_g (°C)
HEMA	1	125	53	193	-11.7
HEA	1	115	51	200	-14.5
GMA	1	442	142	90	13.8
AMA	1	204	78	186	-9.5
EGDMA	2	771	160	70	18.5
DEGDMA	2	626	154	88	13.5
TiEGDMA	2	520	150	113	10.2
TeEGDMA	2	420	140	135	6.5

F = functionality; YM = Young's modulus; TS = tensile strength at break; E = elongation at break.

TABLE VII
Effect of Monomer Concentration on Tensile Properties of Cured Films in
Oligomer-Monomer Systems

Monomer	Wt%	YM (kg/cm ²)	TS (kg/cm ²)	E (%)	T _g (°C)
HEA	5	225	80.5	170	-5
	10	131	64	178	-10
	30	73	47	220	-18
AMA	5	290	96	168	0.5
	10	270	86	175	-4
	30	150	68.4	200	-13
TtEGDMA	5	360	116	156	7
	10	415	126.5	141	8.5
	30	635	175	80	11.5

the monomer concentration, the greater the response of the tensile properties of cured films. Therefore, the properties of films changed by reactive monomers depend on the functionality, end group, chain length, and concentration of monomer.

Thermal Stability of Oligomer-Monomer Systems

Thermogravimetric Analysis (TGA) results of cured films made from 80% oligomer and 20% monomer are shown in Figures 6 and 7. All monomers raise the thermal stability of films as compared to oligomers, except dimethylaminoethyl methacrylate monomer. In the monofunctional monomer systems, the GMA system has the highest decomposition temperature followed

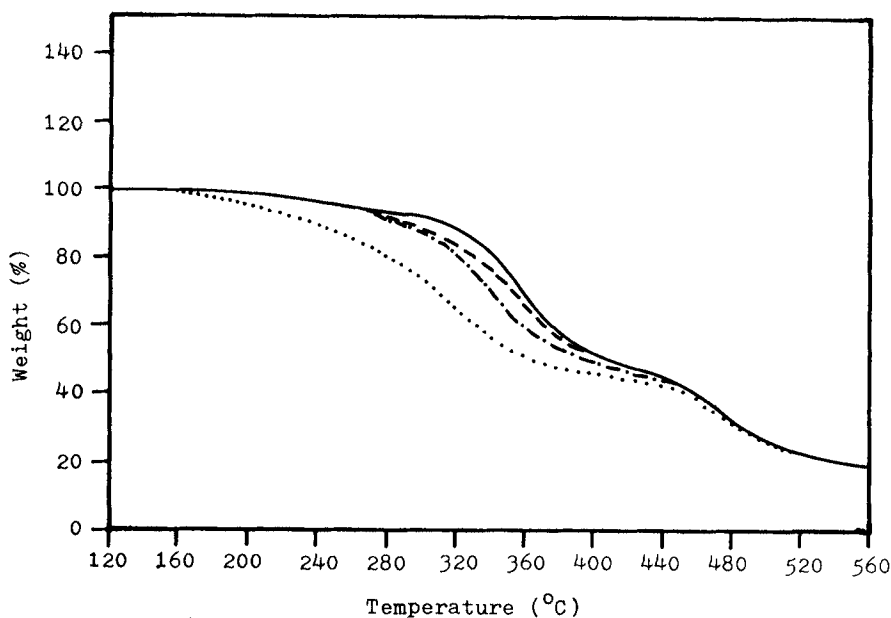


Fig. 6. Effect of monofunctional monomers on thermal stability of cured films in oligomer-monomer systems: (-----) HEMA; (-·-·-) HEA; (—) GMA; (·····) AMA. Oligomer/monomer = 80/20 by weight.

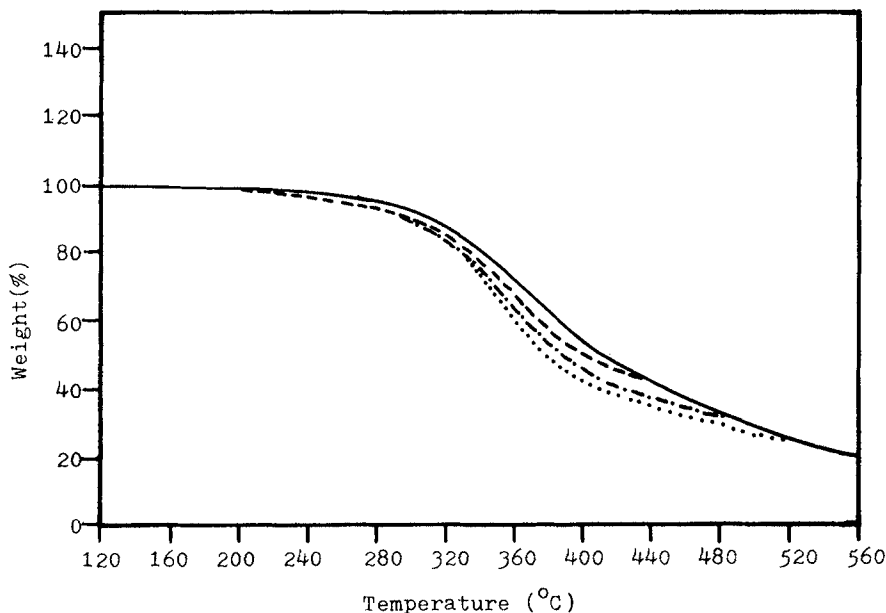


Fig. 7. Effect of difunctional monomers on thermal stability of cured films in oligomer-monomer systems: (—) EGDMA; (---) DEGDMA; (-·-·-) TiEGDMA; (·····) TeEGDMA.

by the HEMA and HEA system, and the AMA system has the lowest decomposition temperature (T_d). As for the AMA system, the lowest T_d of cured film might be caused by the weaker C—N bond of the AMA monomer. In the case of difunctional monomers, a decreasing chain length between two methacrylate groups causes an increase in crosslinking density and thermal stability of the films. The thermal stability of the systems shows the following order: EGDMA > DEGDMA > TiEGDMA > TeEGDMA.

CONCLUSION

Several BTDA-based autocurable polyurethane methacrylates are cured rapidly by UV radiation in the absence of photoinitiator. Increasing polarity of polyols leads to a higher viscosity of oligomer and T_g of cured material. Among prepared oligomers, the polydiethylene hexamethylene-dicarbamate-based material has the highest value of Young's modulus, storage modulus, and T_g , followed by polydiethylene maleate and polydiethylene succinate-based material; the polyethylene glycol-based sample having the lowest value. In addition, the polydiethylene hexamethylenedicarbamate-based sample has strong and tough properties and good breaking strength and elongation.

The addition of monomers reduces the viscosity of systems effectively and provides a wider range of properties. The curing rate is mainly affected by the reactivity of monomers; for example, the system containing HEA monomer has the fastest curing rate and highest gel content at short irradiation time among the monomers. However, the tensile properties and T_g of cured films are related to chemical structure and functionality of monomers. The addition of difunctional monomers gives the films high tensile strength, Young's modulus, and T_g as compared to neat oligomer, but the addition of monofunc-

tional monomers exhibits the opposite behavior. In addition, increasing the monomer concentration will increase the response of tensile properties and T_g of cured films.

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