Reactive Diluents and Properties of Ultraviolet-Cured Polycarbonate Urethane Acrylates

VADIM V. KRONGAUZ* and ANTHONY J. TORTORELLO

DSM Desotech Inc., 1122 St. Charles Street, Elgin, Illinois 60120

SYNOPSIS

Polymer films obtained from photocurable formulations were investigated by tensile methods and dynamic mechanical analysis. The polymer formulations contained photoinitiator, urethane diacrylate oligomer, and acrylic reactive diluent. It was found that diluent concentration may strongly affect the glass transition temperature and elastic modulus of the cured coating. When the diluent homopolymer glass transition temperature is larger than that of oligomer homopolymer, the glass transition temperature and elastic modulus of the coating film increase with the increase of the diluent concentration. When the diluent homopolymer has lower glass transition temperature than the homopolymer of the oligomer, the increase in diluent concentration leads to a decrease in glass transition temperature and elastic modulus of the UV-cured coating film. The effect of the testing temperature on tensile storage modulus of the films containing different concentrations of reactive diluents was studied as well. The data indicated that a variety of coatings with wide ranging but predictable properties can be formulated from previously examined starting materials but used at different concentrations. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The influence of random copolymerization on the properties of the resulting polymers is extensively investigated and widely used in materials design.[1] The addition of copolymerizing monomer disrupts or improves the regularity of the chains shifting the temperatures of polymer melting and glass transition. As the concentration of one of the copolymerizing monomers in the polymerizing formulation increases, the contribution of the others into overall properties of the copolymer becomes less noticeable. Usually the glass transition temperature of the copolymer changes monotonically with the change in concentration of the copolymerizing monomers from 0 to 100% between those of pure homopolymers. Polymer mechanical stiffness measured at certain temperatures, increases with the increase of the glass transition temperature (T_g). Therefore, it appears, that the mechanical properties of a copolymer can be predesigned by the proper selection of the glass transition temperature of the homopolymers formed by diluent monomers used in the formulation.

Ultraviolet (UV) curable coatings of high T_g also exhibit superior stiffness at room temperature.[2] This property was successfully used in formulation of high modulus protective UV-curable fiber-optic coatings.[3,4] To achieve a high modulus polymer film, reactive diluents with a homopolymer T_g in excess of 55°C were copolymerized with polyurethane acrylate oligomers. It was demonstrated that adding a copolymerizing monomer (reactive diluent) capable of forming high T_g homopolymer to the lower T_g oligomer increases the film stiffness.[3,4] However, no attempt was made at the time to quantify the reactive diluent concentration effects.

The effect of copolymerization with various concentrations of reactive diluent on the stiffness of UV-cured epoxyacrylate formulations used as protective optical fiber coatings was investigated recently.[5] In these studies the change in polymer stiffness was measured for polymers formed with 15–35% of ethylhexyl acrylate diluent added to the mixture of the epoxyacrylate oligomers. Ethylhexyl acrylate forms a homopolymer with a T_g of −50°C.[6] The reported trend was a decrease in elongation and

Table I Monomers Used as Diluents in Formulations

Reactive Diluent (Monomer)	Abbreviation	Homopolymer T_g (°C)	Reference
n-Butyl acrylate	BAC	-55	6
Cyclohexyl acrylate	CHA	16	6
N-(iso-butoxymethyl)acrylamide	IBMA	30	6
Isobornyl acrylate	IBOA	94	6

an increase in tensile modulus with increasing ethylhexyl acrylate content in the formulation.[5] This would not be expected in light of the previous studies.[3,4] However, in the reported work,[5] the glass transition temperature of the copolymer was not measured, and the results of the mechanical testing were not correlated with the glass transition temperature of the diluent's homopolymer or with the cured copolymer T_g.

Several other investigations dealt with the effect of relative concentration of oligomer and diluent on the properties of the UV-cured polyglycol diacrylates.[7-9] The change in UV-cured polymer T_g, tensile strength, and formulation viscosity were observed with a change in oligomer–diluent ratio, however, no correlation with the glass transition temperature of the component homopolymers or with the concentration of the components was attempted.

The elastic modulus was correlated with the ratio of the diluent–oligomer concentration in epoxy–acrylate UV-curable polymers over a limited concentration range.[10] Again, the properties of the homopolymer of a diluent or oligomer were not clearly correlated with the properties of the cured film.

The concept of regulating the properties of protective coatings by "a simple change of active diluent concentration in the liquid formulation" with predictable results as proposed by Rayss et al.[5] is extremely appealing in the current industrial climate. Indeed, such alterations may not require reevaluation of the product's environmental and toxicological impact and will not demand recertification of the raw materials used in the formulations.

We investigated the reactive diluent effects on UV-curable coatings based on laboratory synthesized polycarbonate urethane diacrylate oligomers. Our goal was to determine whether small molecular weight acrylate monomers can significantly alter the properties of coatings based predominantly ($\sim$ 75%) on high molecular weight (> 2000 au) flexible oligomer. It was of particular interest to establish to what extent the glass transition temperature of the diluent homopolymer affects the properties of the copolymerized oligomer–polymer mixture. Elastic modulus,

glass transition temperature, and elongation of the cured polymer films were measured. The results of these investigations are presented below.
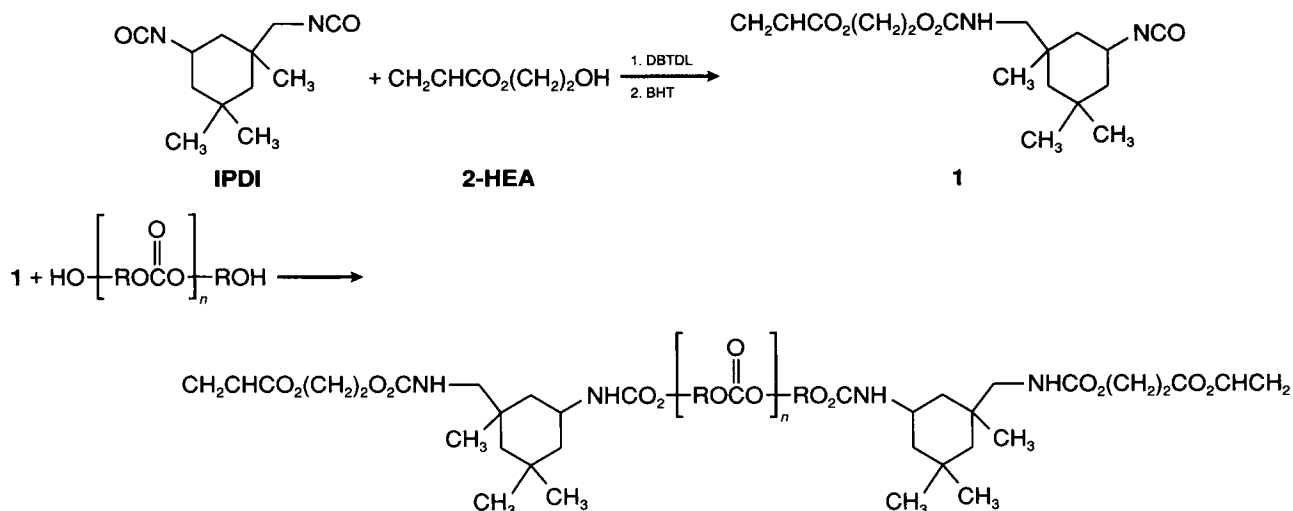
EXPERIMENTAL

Materials

The UV-curable formulations used in the current work were similar to those patented previously.[3,4] Formulations consisted of diacrylated polycarbonate urethane oligomer dissolved in the liquid acrylate monomer (reactive diluent) in the presence of 2% photoinitiator (2,2-dimethoxy-2-phenylacetophenone, Irgacure 651®, Ciba–Geigy Corp.). Reactive diluents used in the study (Table I) were all purchased from Aldrich Chemical Company.

Oligomer Synthesis

The polycarbonate urethane acrylate oligomer was synthesized using a modification of the previously reported procedure.[11] The reaction sequence is outlined in Scheme 1.

A 500-mL four-neck, round-bottom flask equipped with mechanical stirrer, thermometer, reflux condenser (connected to a bubble tube), and inlet line for dry air was used. Weighed into the flask were 109.11 g (0.4908 mol) of isophorone diisocyanate (IPDI, Huls America), 0.23 g (0.36 mmol) of dibutyltin dilaurate (DBTDL, OM Group), and 0.12 g (0.54 mmol) of 2,6-di-tert-butyl-4-methylphenol (BHT, Fitz Chemical). The flask contents were stirred at room temperature under an atmosphere of dry air until completely dissolved. Then 56.99 g (0.4908 mol) of 2-hydroxyethyl acrylate (2-HEA, Dow Chemical) was then added dropwise. The addition was controlled to occur over 60–90 min at 35°C. An external ice bath was used for temperature control.

After addition was completed, the mixture was warmed to 40°C and held for 1 h. At this point, the isocyanate content was measured by reaction with a calculated excess of dibutylamine and back titra-

OCN — NCO

CH$_3$

CH$_3$ CH$_3$

IPDI

+ CH$_2$CHCO$_2$(CH$_2$)$_2$OH

2-HEA

1. DBTDL
2. BHT

CH$_2$CHCO$_2$(CH$_2$)$_2$O$_2$CNH — NCO

CH$_3$

CH$_3$ CH$_3$

1

$$1 + HO\left[ROCO\right]_n ROH \longrightarrow$$

CH$_2$CHCO$_2$(CH$_2$)$_2$O$_2$CNH — NHCO$_2$$\left[ROCO\right]_nRO_2$CNH — NHCO$_2$(CH$_2$)$_2CO_2$CHCH$_2$

CH$_3$

CH$_3$ CH$_3$

CH$_3$

CH$_3$ CH$_3$

Scheme 1. Polycarbonate urethane acrylate synthesis.

tion with standardized (0.1N) HCl solution. When the theoretical value was obtained, the polycarbonate diol was added.

The polycarbonate diol is generally described as a copolymer of 1,6-hexane diol and an ether. Because the polycarbonate diol was a solid at room temperature, it was melted (usually at 60°C) prior to addition. The flask contents were then warmed to 60°C and the agitation increased as 218.55 g (0.2454 mol) of polycarbonate diol was added in one portion. The mixture temperature was allowed to increase to 80°C as a result of an exothermal reaction. The temperature was held at 80°C until the isocyanate content dropped to < 0.1% (approximately 12 h). The resulting viscous liquid was poured into a lined can for storage and use.

Formulations

The following reactive diluents (monomers) were used in the formulations at concentrations ranging from 15 to 50% in 5% increments: cyclohexyl acrylate (CHA, Polysciences Inc.), N-isobutoxymethyl acrylamide (IBMA, Polysciences Inc.), n-butyl acrylate (BAC, Aldrich Chem. Co.), and isobornyl acrylate (IBOA, Radcure Specialties). The reactive diluents were used as supplied without further purification. The monomer was added into the oligomer and the mixture was heated to 60°C for 2 h and shaken until homogeneous.

Film Preparation and Testing

The formulations were coated onto polished glass plates (8 × 11 in.) using a 75-μm doctor knife (Bird & Sons Co.). The coating formulations were preheated to 60°C in an electric oven and the glass plates were preheated with a hot air blower immediately prior to the coating application. The coating knife was exposed to a hot air stream to prevent an increase in coating viscosity during the application. The films were cured at 1 J/cm^2 (D-lamp, Fusion Systems), under an ~ 360 L/min flow of dry nitrogen. All films were cured to < 10% of residual acrylate unsaturation as measured by FTIR on both film surfaces.

Strips of coatings, 1.3-cm wide, were cut and tested for tensile properties. The testing was conducted using the Instron® system Model 4201 interfaced with a personal computer.

A 5.1-cm gage length with a 2.54-cm/min strain rate was employed. Modulus of elasticity was determined using a secant method at 2.5% elongation under controlled temperature (23 ± 0.5°C) and humidity (50 ± 5% RH).

Dynamic mechanical analysis (DMA) of the cured films[7-10,12,13] was conducted in a tensile mode on a Rheometrics RSA-II system after the samples were annealed at 80°C for ~ 5 min in a nitrogen atmosphere at 0% RH to remove water and other volatiles. Then the temperature was lowered in 20°C steps to the starting temperature of the run. The testing was conducted at 0% RH under nitrogen

flow. All tests were made at the frequency 1 rad/s (0.16 Hz). Strain was set at 0.001 at low temperature and increased automatically under instrument control to a maximum of 0.01 at the high temperature end. The heating rate was ≈ 1°C/min. The annealing procedure precluded the DMA testing of IBMA, because IBMA is subjected to thermal ionic polymerization at this temperature. The ratio between the energy dissipated into heat and the stored elastic energy of the cured polymer film is called the loss factor, tan(δ), and was measured as a function of temperature. Tensile storage modulus, E', of the cured film was measured as well (Fig. 1). The temperature at which the loss factor, tan(δ), reached the maximum was used as the glass transition temperature of the sample polymer.

RESULTS AND DISCUSSION

Mechanical testing showed that the reactive diluent altered the properties of the UV-cured polymer film, even when the formulation contained flexible, high molecular weight oligomer (Fig. 2). When the polymer film was prepared using diluent forming a homopolymer with T_g < 16°C, the elastic modulus of the polymer decreased with the increase of the diluent concentration. When a diluent with a homopolymer T_g > 16°C was used, the elastic modulus of the cured film increased with increasing diluent concentration (Fig. 2). The room temperature elastic modulus of the cured film also increased with the T_g of the diluent homopolymer at constant diluent concentration (Fig. 2). This increase in elastic modulus with the increase of T_g of the reactive diluent homopolymer is more noticeable at higher concentrations of the reactive diluent (Fig. 2, Table II).

The dependence of the loss factor on temperature and on the diluent concentration was recorded. It was found that the maximum of the tan(δ) vs. temperature curve shifted toward the higher temperatures for increasing concentration of IBOA diluent [Fig. 3(a)], remained the same for all of the CHA diluent concentrations [Fig. 3(b)], and shifted toward the lower values for the increasing concentrations of the BAC diluent [Fig. 3(c)].
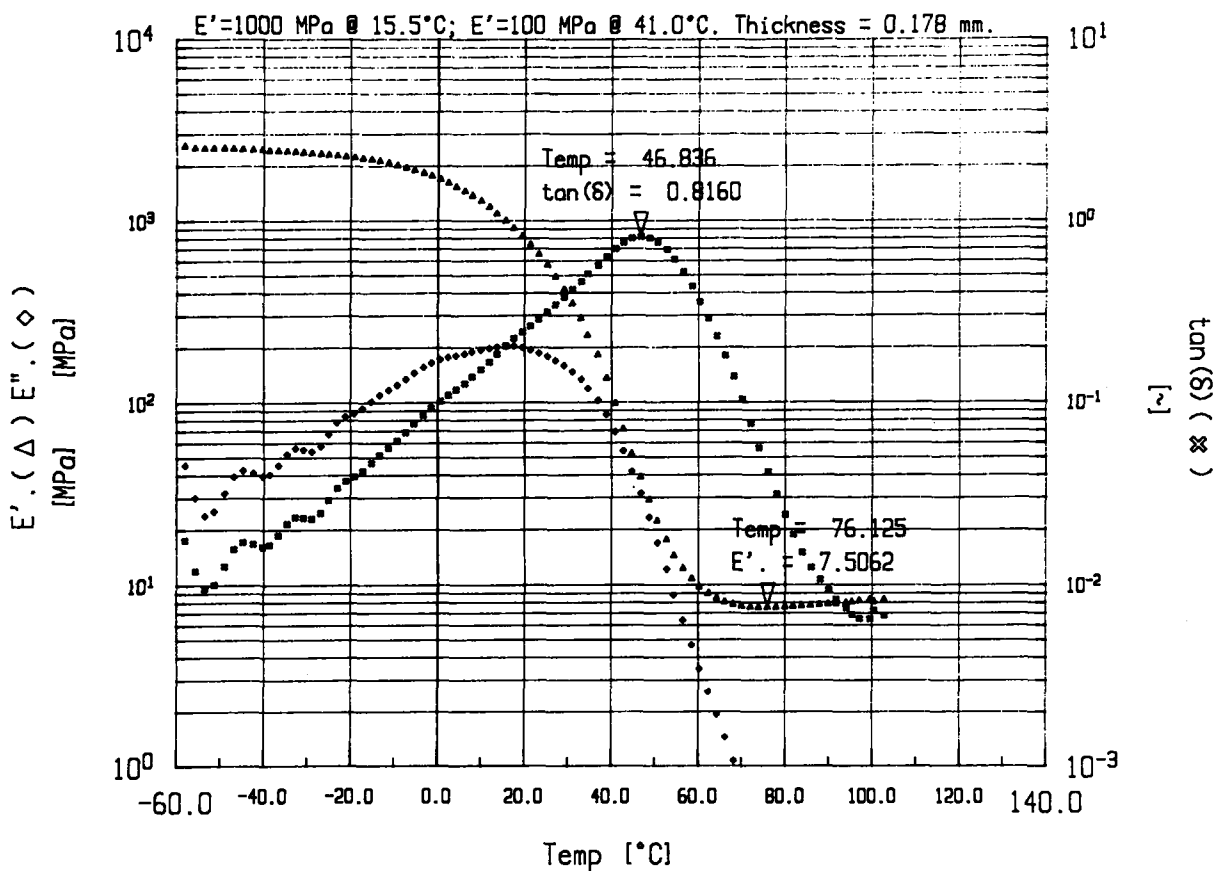

Figure 1 Typical results of dynamic mechanical analysis of the studied polyurethane acrylate films: formulation containing 20% isobornyl acrylate reactive diluent.
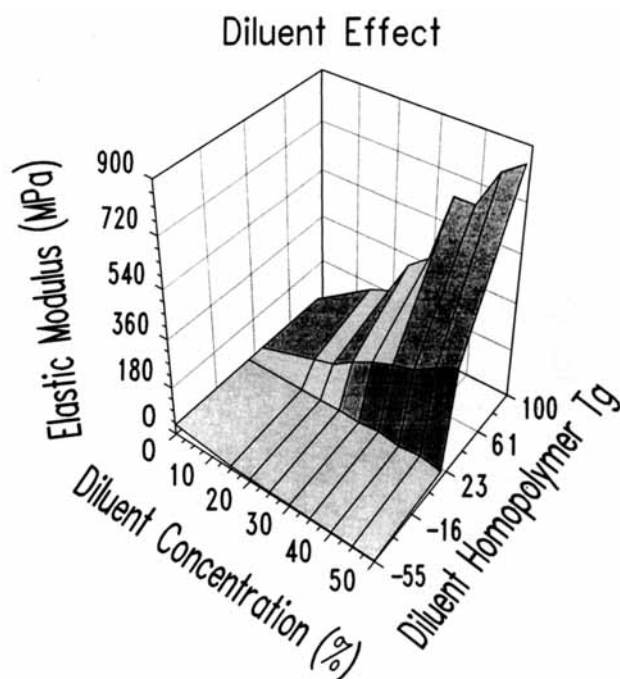
Diluent Effect

Figure 2 Dependence of elastic modulus measured at 23°C using an Instron® tester on diluent concentration and diluent homopolymer glass transition temperature.

UV curing and testing of neat oligomer and neat diluent films was prohibitively difficult. To bypass this difficulty the method developed for measuring the crystallization temperature[1] was applied. The method relies on extrapolating the polymer properties to zero additive concentration. Because the glass transition temperature of the film did not vary with the change of CHA concentration, the literature cited value[6] of 16°C would seem to be a proper choice for the glass transition temperature of the oligomer.

However, DMA testing of the cured films containing CHA diluent showed that tan (δ) reached its maximum value (within experimental error) at 32.5°C for all CHA concentrations studied. Therefore, 32.5°C was accepted as the glass transition temperature of the cured neat oligomer as tested by DMA. In data processing, the glass transition temperature of the reactive diluent homopolymers published previously was used (Table I). The glass transition temperature of the UV-cured copolymer film was measured as a function of the reactive diluent concentration and reactive diluent homopolymer glass transition temperature (Fig. 4).

The glass transition temperatures of the polymer films prepared with different concentration ratios of oligomer and diluent exhibited behavior similar to the elastic modulus of the same films discussed above (Figs. 2, 4). That is, when the reactive diluent forming high T_g homopolymer (> 16°C) was used, the copolymer T_g increased with the diluent concentration increase. Reactive diluent forming homopolymer with reported T_g < 16°C, yielded copolymer that exhibited decreasing T_g with increasing diluent concentration (Fig. 4). Glass transition temperature of the cured film also increased with the increase of the glass transition temperature of the diluent homopolymer (Fig. 4, Table III). The "rate" of increase was greater at higher concentrations of the reactive diluent (Fig. 4).

The elastic modulus dependence on reactive diluent concentration and on diluent homopolymer T_g obtained using Instron® tensile testing correlated qualitatively with the DMA monitored cured film T_g dependence (Figs. 2, 4, Tables II, III). Urethane diacrylate oligomer based UV-cured polymers containing diluents with higher homopolymer T_g ex-

Table II   Room Temperature Mechanical Properties of the Photocured Polymer Films (Instron® Test)

Concentration of Diluent (%)	BAC (T_g − 55°C)	CHA (T_g 16°C)	IBMA (T_g 30°C)	IBOA (T_g 94°C)
	Reactive Diluent			
	Young's Modulus (MPa)			
15	11.6	38	110	184
20	9.3	38	132	214
25	7.6	41	181	351
30	6.7	36	219	409
35	5.4	44	250	666
40	4.7	32	274	666
45	4.0	40	322	806
50	3.4	27	363	859

Isobornylacrylate Monomer

Cyclohexylacrylate Monomer
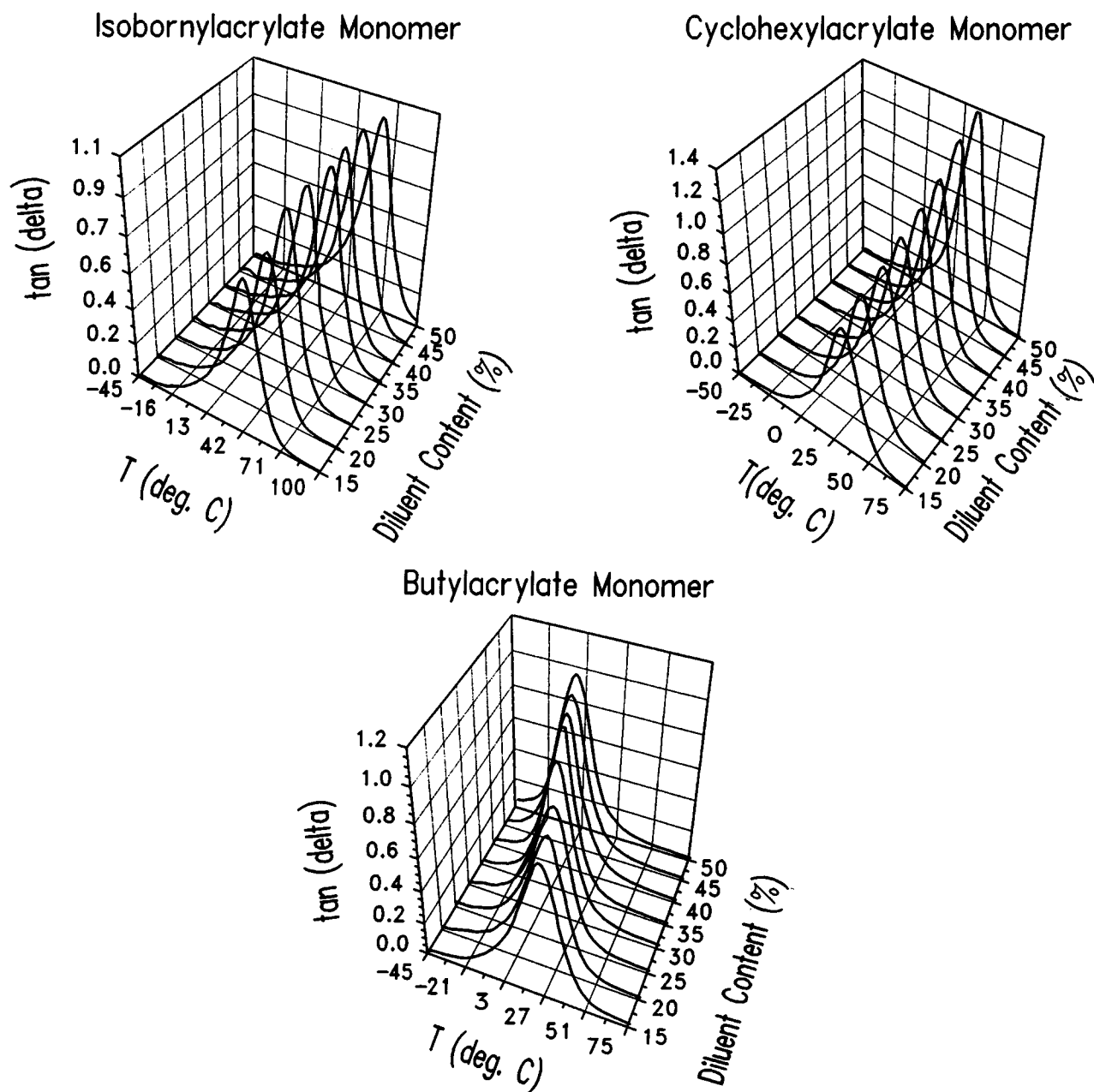
Butylacrylate Monomer

Figure 3 Dependence of cured coating loss factor, tan(δ), on temperature and diluent concentration in coating formulation: (a) isobornyl acrylate diluent; (b) cyclohexyl acrylate diluent; and (c) butyl acrylate diluent.

hibited higher elastic modulus than corresponding formulations containing diluents with the lower T_g. The Instron® measured tensile modulus increase with the T_g of the cured film (Fig. 5). The rate of the modulus change increased with increasing T_g (Fig. 5). Thus, for BAC-based coatings, a 30°C change in T_g corresponded to a change in elastic modulus of 8.2 MPa (a factor of 3.4); for the coatings containing IBOA, a 18.5°C change in T_g resulted in

a modulus change of 675 MPa (a factor of 4.7). Although further investigations are required, we considered some of the factors that could lead to nonlinear dependence of polymer modulus on polymer glass transition temperature.

The glass transition temperature value often depends on the measurement technique.[14] DMA analysis used in this study indicated that the glass transition temperature of polymerized neat oligomer was
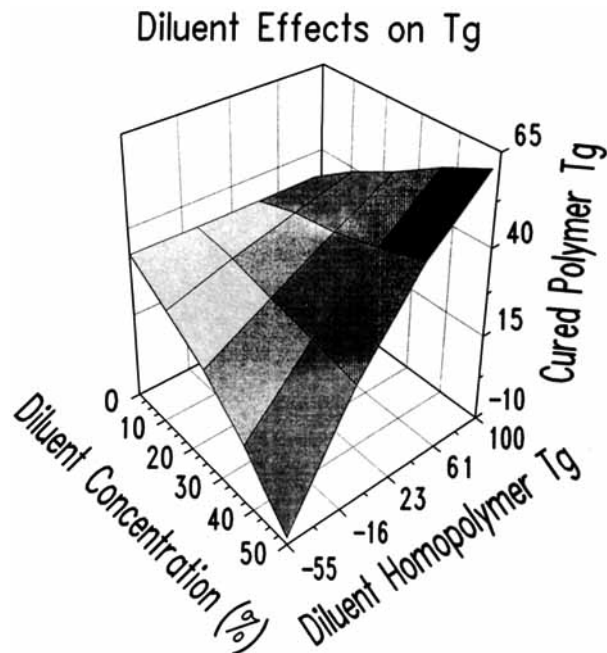
Diluent Effects on Tg

Figure 4 Dependence of the DMA measured glass transition temperature of UV-cured coatings on reactive diluent homopolymer T_g, and diluent concentration in the coating formulation.

equal to that of CHA homopolymer, and equal to about 32.5°C. The published glass transition temperature for CHA homopolymer was 16°C. Knowing the T_g of the copolymer, one can recompute the T_g of a diluent's homopolymer using eq. (1). This equation, known as the Fox equation, describes an empirical relation between the glass transition temperature and weight fraction of copolymerizing monomers [eq. (1)][1,15,16]:

$$(T_g)^{-1} = w_1(T_{g1})^{-1} + w_2(T_{g2})^{-1} \quad (1)$$

where w_i and T_{gi} are the weight fraction and homopolymer glass transition temperature (absolute temperature scale, Kelvin) of the comonomer i, respectively. Equation (1) yields 96.6°C for IBOA homopolymer, if oligomer $T_g = 32.5$°C. The same computations result in BAC homopolymer $T_g = -32.6$°C rather than −55°C. Whether the published data or data computed using an empirical formula [eq. (1)] is considered, the change in homopolymer glass transition temperature from neat oligomer to the neat diluent is larger for IBOA than for BAC, which is to be expected considering the observed effect of low T_g diluent (Fig. 5).

Clearly, one can use the dependence of the modulus on T_g (Fig. 5) to deduce the glass transition temperature of the coating, knowing its elastic modulus. Such

Table III Glass Transition Temperature of Photocured Polymer Films

| Concentration of Diluent (%) | Reactive Diluent | | |
| | BAC (T_g − 55°C) | CHA (T_g 16°C) | IBOA (T_g 94°C) |
	T_g (°C) from tan (δ)		
15	23.9	32.8	43.0
20	21.6	31.5	46.8
25	13.4	32.5	47.6
30	11.8	31.5	50.2
35	8.6	32.6	55.5
40	4.2	32.8	54.6
45	0.0	33.4	57.5
50	−8	33.8	61.5

derivation is valid in cases such as the one presented in this work. The elastic modulus dependence on temperature is well investigated (Fig. 1).[1] The Williams–Landel–Ferry (WLF) equation[1,17] can be used to relate tensile modulus to glass transition temperature in the polymer coatings (Fig. 5) [eq. (2)]:

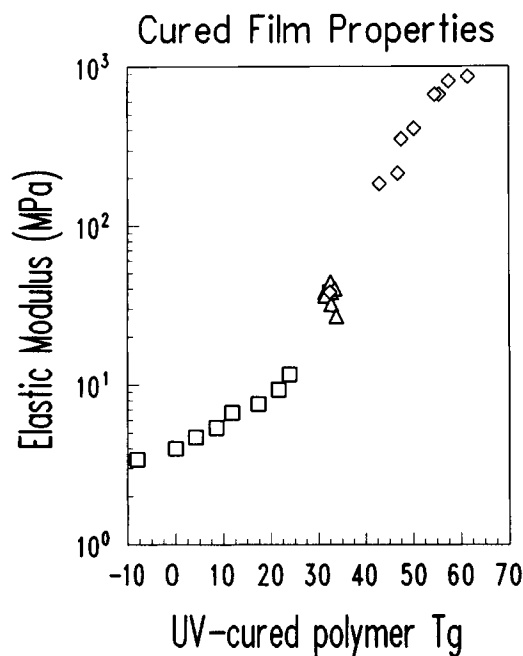$$\log(E/E_o) = -[A(T - T_g)]/[B + T - T_g] \quad (2)$$

Cured Film Properties

Figure 5 Dependence of the elastic modulus measured at 23°C using an Instron® tester on the coating glass transition temperature determined by DMA: (□) BAC; (△) CHA; and (◇) IBOA.

where E is the elastic or tensile modulus at temperature T, E_o is the elastic or tensile modulus at the reference temperature, T_g; and A and B are constant coefficients. It is known that not all polymer systems behave according to the WLF equation. The copolymer films investigated in this work were made by random radical copolymerization of an oligomer with molecular weight $> 1,500$ and a small molecular weight (< 500) reactive diluent. The cured polymers did not exhibit any phase separation or other inhomogeneities. However, experimental measurements were needed to demonstrate predictability of the mechanical properties temperature dependence.

Elastic modulus measurements in this study were conducted at room temperature, $23 \pm 5°C$. Thus, this temperature was considered as a "reference" temperature when T_g was changed. The WLF equation reproduced qualitatively the shape of the elastic modulus dependence on T_g (Fig. 5). The data in Figure 5 demonstrated that change of reactive diluent did not alter the randomness of the copolymerization. Indeed, polymers made with different reactive diluents seemed to be described by a single WLF type curve (Fig. 5). This finding indicated that viscoelastic properties of the UV-cured films were determined by the high molecular weight difunctional oligomer, while the temperature shift of the properties could have been controlled by the small molecular weight diluent. The reason for such performance of the copolymer must be further investigated.

The temperature shift in tensile storage modulus values with the shift of the cured film glass transition temperature may be illustrated using the modulus temperature dependence obtained by DMA (Fig. 6). The curve in Figure 5 (if the elastic and tensile storage moduli are equivalent) represented a cross section of the surface describing modulus dependence on T and T_g at a constant T equal to room temperature. Figure 6 illustrates that the shape of the dependence of modulus on the polymer T_g changed depending on the temperature at which the moduli were measured. It was not clear whether the same WLF coefficients A and B [eq. (2)] apply to the entire range of temperatures and T_g. However, it did appear that the values of elastic modulus for coatings with $T_g > 298$ K (room temperature), increased faster than those for coatings with lower T_g when measured at 298 K. This changed when the measurements of moduli were conducted at higher temperatures (Fig. 6). The general trend of modulus increase with T_g increase remained even for very low testing temperatures. It was long postulated that
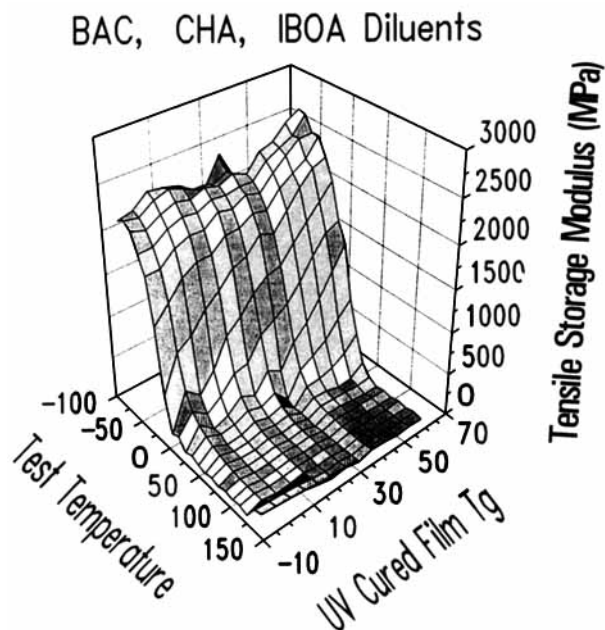

Figure 6   DMA results: dependence of the tensile storage modulus of the cured coating on temperature and coating glass transition temperature.

polymers with higher T_g exhibit higher elastic modulus. However, to the best of our knowledge, a direct and quantitative experimental demonstration of this effect (Figs. 5, 6) was not previously documented for UV-cured polymers.

Equation (2) predicted the observed nonlinearity of modulus dependence on the glass transition temperature of the polymer. At temperatures above T_g an increase in diluent homopolymer T_g also led to the cured film modulus increases (Figs. 5, 6). Apparently, the diluent affected the properties of the cured polymer, such as the extent of crosslinking and the alignment and interaction between the polymer chains.[1] Further experimental and theoretical work is required to understand the nature of these effects at temperatures below that of the polymer glass transition. Perhaps elasticity of the bridging chains can be correlated with the reactive diluent properties and concentration. Although the observed behavior requires further experimental and theoretical analysis, it can be successfully used in design of the polymer coatings. Indeed, a relatively small change in oligomer or reactive diluent can produce an entirely new material.

The tensile strength and maximum elongation at the break of cured polymer films were also measured for various coating compositions (Table IV). There was a difference in elongation at break and tensile strength of the films containing different diluents. Thus, the tensile strength of the polymer containing

BAC was in the range of 1–10 MPa; compositions with CHA yielded strength in the range of 16–23 MPa; IBMA compositions yielded 18–22 MPa; and IBOA-based materials had tensile strength in the range of 23–31 MPa. The elongation at break point varied from 48 to 114% for BAC-based polymers, 123 to 166% for CHA, 111 to 155% for IBMA, and 67 to 130% for IBOA-containing films (Table IV). The variation in tensile strength and the elongation at break for most of the studied diluents (excluding BAC) was less sensitive than the elastic modulus to the type of diluent used and to the change in diluent–oligomer ratio in formulation. Perhaps at a break point the elongation and tensile strength were controlled by oligomer composition. Further investigation of elongation at break dependence on the polymer structure is required.

CONCLUSION

The mechanical properties of UV-cured polyurethane acrylate films were studied as a function of composition and glass transition temperature. The formulations consisted of bifunctional oligomer, monofunctional reactive diluent, and photoinitiator. The glass transition temperatures of the cured polymers with a wide range of diluent and oligomer ratios were measured using DMA. It was determined that the concentration of the reactive diluent strongly affected the glass transition temperature and elastic modulus of the UV-cured polymer (Figs. 2–4). The magnitude of the diluent concentration effect was dependent on the difference, ΔT, between the glass transition temperatures of the reactive diluent and oligomer homopolymers. The elastic modulus of the cured polymer increased with the increase of the diluent concentration for $\Delta T > 0$, remained the same for $\Delta T = 0$, and declined when $\Delta T < 0$. It was also determined that elastic modulus increased nonlinearly with the increase in T_g of the cured copolymer (Figs. 5, 6), as predicted by WLF equation.

It became apparent after these investigations that the properties of photocured polymers could be altered to suit the particular industrial specification without a drastic change in coating composition. A relatively minor change in diluent concentration of an existing commercial coating formulation could be used to provide a suitable candidate for an alternative application. Because this approach should not require new toxicological or environmental impact investigation, the altered coating may be commercialized in a shorter time. The change in properties was reproducible and predictable on the basis of oligomer and diluent homopolymers glass transition temperatures and relative concentrations.

Table IV Tensile Strength and Elongation at Break of Photocured Polymer Films

	Reactive Diluent							
	BAC ($T_g - 55°C$)		CHA (T_g 16°C)		IBMA (T_g 30°C)		IBOA (T_g 94°C)	
	Elongation Strength							
Concentration of Diluent (%)	%	(MPa)	%	(MPa)	%	(MPa)	%	(MPa)
15	113 ± 8	10.3 ± 1.9	133 ± 7	18 ± 3	129 ± 8	22 ± 3	118 ± 8	25 ± 3
20	114 ± 14	7.2 ± 2.0	113 ± 4	18 ± 2	111 ± 17	18 ± 4	125 ± 6	26 ± 3
25	97 ± 6	4.5 ± 0.5	123 ± 3	18 ± 2	129 ± 12	21 ± 3	130 ± 9	31 ± 4
30	68 ± 7	2.7 ± 0.3	125 ± 10	15 ± 3	135 ± 14	22 ± 4	130 ± 14	31 ± 5
35	74 ± 14	2.5 ± 0.5	148 ± 5	21 ± 2	142 ± 10	22 ± 3	80 ± 20	23 ± 3
40	70 ± 11	2.0 ± 0.3	156 ± 7	22 ± 3	138 ± 19	20 ± 3	100 ± 3	24 ± 2
45	67 ± 13	1.7 ± 0.3	166 ± 14	23 ± 7	143 ± 18	21 ± 4	88 ± 17	26 ± 1
50	48 ± 0.7	1.0 ± 0.1	162 ± 8	16 ± 3	155 ± 11	20 ± 2	67 ± 13	27 ± 1

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