

# Comparative Study of Electron-Beam- and Ultraviolet-Cured Films of Urethane Acrylate

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## SYNOPSIS

A urethane diacrylate oligomer was used to develop 40 different formulations in combination with eight different reactive diluents in the presence of five different coadditives. Thin films were prepared with these formulated solutions under ionizing radiation using either electron beam (EB) or ultraviolet (UV) rays. In the latter case, a photoinitiator was incorporated into the formulation. Physical, mechanical, and thermal properties of the cured films were studied. Tensile properties (strength and elongation) were almost double with the UV-cured films than those of the EB-cured films. Thermal behavior was also observed to be different in these two systems. These properties were correlated with the glass transition temperatures of the homopolymer of codiluents used. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Urethane acrylate prepolymer is considered to be a unique oligomer compared to polyester and epoxy oligomers in the preparation of thin films for specific utilities. Recently, a number of workers has reported on the preparation of thin films with a urethane acrylate oligomer in the presence of different diluents and codiluents using either an electron beam<sup>1-3</sup> or ultraviolet rays.<sup>4-10</sup> Physical, mechanical, and thermal behaviors of some of these reported works have been correlated with glass transition temperatures of the reactive diluents used in these systems. Each of the constituents (oligomer, diluent, and codiluent) used in the formulations has distinct properties related to its physical and chemical characters that are dependent on the respective structural shape and arrangement of the functional groups present in the molecule. The structural shape and geometry of the molecule of the copolymer (thin film) prepared out of the formulated solution of oligomers, diluent, and codiluent are new and completely different from those of each of its constituents. Thus, the characteristic properties of the co-

polymer were correlated to the glass transition temperature ( $T_g$ ) of the reactive diluent, because the  $T_g$  is very much related to the geometry and structural shape of the molecule.

The present work reports on the relationship of physical, mechanical, and thermal behaviors of the thin films (copolymer) with the glass transition temperature ( $T_g$ ) of the codiluents used in the formulations. The change of these behaviors under UV and EB curing is also elaborated in order to differentiate between two radiation processing systems.

## EXPERIMENT

### Materials

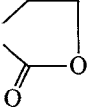
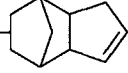
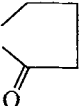

Urethane diacrylate, an aromatic-based prepolymer containing two acrylate groups at both ends of the molecule, was procured from Aronix Co. Eight reactive diluents and five codiluents (Table I) of different  $T_g$ s were used as received from E. Merck. Darocur 1173 was used as the photoinitiator in the case of the ultraviolet radiation system.

### Methods

Solutions were formulated as oligomer : diluent : codiluent = 50 : 25 : 25, w/w; but when a photoin-

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**Table I** Structural Formula and  $T_g$  of Oligomer, Diluent, and Codiluent

Name	Structure
<b>Oligomer</b>	
Aromatic urethane diacrylate (M1100), $T_g = 47^\circ\text{C}$	$\text{CH}_2=\text{CH}-\text{CO}-\text{O}-\text{R}'-\text{O}-\text{O}-\text{CNH}-(\text{R}-\text{NHCO}-\text{O}-\text{polyol}-\text{O}-\text{CO}-\text{NH})_n-\text{R}-\text{NH}-\text{CO}-\text{O}-\text{R}'-\text{O}-\text{CO}-\text{CH}=\text{CH}_2$
<b>Diluents</b>	
2-methoxy ethyl acrylate (MEA), $T_g = -110^\circ\text{C}$ , MW = 130	$\text{CH}_2=\text{CH}-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3$
2-Hydroxy ethyl acrylate (HEA), $T_g = -15^\circ\text{C}$ , MW = 116	$\text{CH}_2=\text{CH}-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2\text{OH}$
2-(2-oxo-3-oxazolidinyl)ethyl acrylate (CL959), $T_g = 12^\circ\text{C}$ , MW = 185	$\text{CH}_2=\text{CH}-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-\text{N}$ 
<i>N</i> -butyl carbamate ethyl acrylate (CL1039), $T_g = 16^\circ\text{C}$ , MW = 215	$\text{CH}_2=\text{CH}-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{NH}-\text{C}_4\text{H}_9$
Tripropylene glycol diacrylate (TPGDA), $T_g = 90^\circ\text{C}$ , MW = 300	$\text{CH}_2=\text{CH}-\text{O}-(\text{OC}_3\text{H}_6)_3-\text{O}-\text{CO}-\text{CH}=\text{CH}_2$
Dicyclopentanyl acrylate (DPA), $T_g = 120^\circ\text{C}$ , MW = 204	$\text{CH}_2=\text{CH}-\text{CO}-\text{O}$ 
<i>N</i> -vinyl pyrrolidone (NVP), $T_g = 175^\circ\text{C}$ , MW = 111	$\text{CH}_2=\text{CH}-\text{N}$ 
Trimethylol propane triacrylate (TMPTA), $T_g = 250^\circ\text{C}$ , MW = 296	$(\text{CH}_2=\text{CH}-\text{CO}-\text{O}-\text{CH}_2)_3\text{C}-\text{CH}_2-\text{CH}_3$
<b>Codiluents</b>	
Ethyl acrylate (EA), $T_g = -24^\circ\text{C}$ , MW = 100	$\text{CH}_2=\text{CH}-\text{CO}-\text{OC}_2\text{H}_5$
Methyl acrylate (MA), $T_g = 10^\circ\text{C}$ , MW = 86	$\text{CH}_2=\text{CH}-\text{CO}-\text{OCH}_3$
Cyclohexyl acrylate (CHA), $T_g = 19^\circ\text{C}$ , MW = 154	$\text{CH}_2=\text{CH}-\text{CO}-\text{O}$ 
Vinyl acetate (VAc), $T_g = 32^\circ\text{C}$ , MW = 86	$\text{CH}_2=\text{CH}-\text{O}-\text{CO}-\text{CH}_3$
Tetrabutyl acrylate (t-BA), $T_g = 43^\circ\text{C}$ , MW = 116	$\text{CH}_2=\text{CH}-\text{CO}-\text{O}-\text{C}-(\text{CH}_3)_3$

$T_g$  = Glass transition temperature, taken from polymer Handbook.<sup>12</sup>

itiator (Darocur 1173) was incorporated into the system, the formulation was adjusted as oligomer : diluent : codiluent : photoinitiator = 50 : 24 : 24 : 2, w/w. The latter solution was used in the case of UV radiation, while the former was used for the EB radiation system. The solution was coated on a glass plate (8 × 5 cm) using a bar coater (No. 0.018 in) of Abbey Chemicals Co. (Australia) producing 30 ± 3 μm thick film on the plate. These were then irradiated either under UV or EB radiation.

In the case of UV radiation, a Minicure-UV machine of IST-Technik (Germany) was used.

This delivers a 2 kW dose per pass under the lamp (254–313 nm) at a conveyor speed of 1 m/min. The EB radiation was carried out by using a 60 cm wide Curetron, an electron beam accelerator machine of Nissin-High Voltage Co. (Japan), in a nitrogen atmosphere (oxygen content less than 10 ppm) with an accelerating voltage of 300 keV at 15 mA current with a conveyor speed of 75 m/min. The plates were passed several times under the UV or EB radiation in order to attain the required dose for ensuring the full curing of the coating.

## Film Hardness

The hardness of the UV-cured films only was determined by the pendulum hardness method using a Pendulum Hardness Tester (Labotron, BYKE). The film hardness of the EB-cured films was measured by the Pencil Hardness method (the results are not included in this report). The cured films were then carefully peeled off the plates in order to determine other properties of the film as mentioned later.

## Gel Content

The gel of the cured film was determined by extracting a known weight of the film in hot acetone contained in a Soxhlet apparatus. The difference of weights of the film before and after the extraction determines the gel content.

## Tensile Properties

The tensile properties, particularly strength (TS) and elongation (Eb) at the break, were determined directly with the help of INSTRON (model 1011) at a crosshead speed of 3 cm/min with a load capacity of 500 lbs. The INSTRON has an accuracy margin of 1% and the gauge length was 0.5 inch. The specimen (5 × 1 cm) had a dumbbell shape. The experimental error was very minimum and never exceeded 2% in extreme cases.

## Thermal Property

A 2 kg/cm<sup>2</sup> pressure was applied for folding the cured film at 180°. The brittle films broke while the elastic film got folded; some of them remained folded overnight at the ambient temperature (25°C). However, the deformation could be removed, in some cases, by heating the deformed film at a certain temperature above 25°C for 1 h. This temperature is called the shape recovery temperature.

## RESULTS AND DISCUSSION

Pendulum hardness (PH) of the UV-cured film was measured to determine the film hardness and the UV dose intensity at which the film is properly cured. Figure 1 represents a typical plot of PH values of the UV-cured films of the ethyl acrylate (EA) series in the presence of different reactive diluents against a number of passes under the UV lamp. The PH increases with UV dose, attains maxima (for some

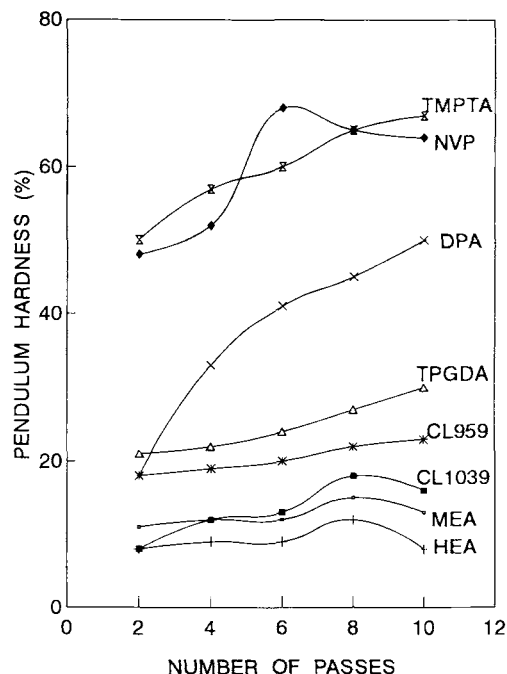
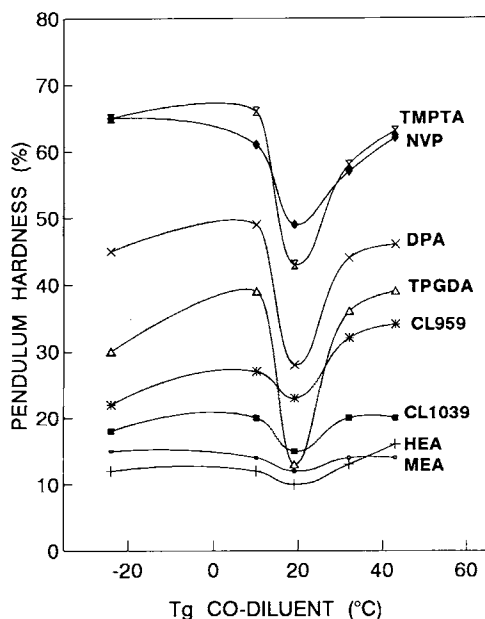


Figure 1 Pendulum hardness is plotted against the number of passes under the UV lamp.

cases), and then decreases. The decrease may be caused by degradation at higher doses. It is observed here, as indicated by others,<sup>4,6,7</sup> that the maximum PH values are obtained between six and eight passes under UV radiation, depending on the nature of formulations. The highest PH values are obtained by the NVP and TMPTA series, followed by the DPAs. The lowest PH values are exhibited by the HEA series. TMPTA has trifunctional acrylated groups and, thus, has branchlike behavior to create more crosslinking among the ingredients of the formulation. It is expected that more crosslinking will yield more film hardness. TPGDA is a difunctional molecule and should have yielded the second highest hardness; but NVP, being a monofunctional diluent, has yielded the PH more than that of the difunctional diluent TPGDA. This is because NVP is a unique molecule<sup>1-3</sup> that contains —N=CO— group capable of creating strong augmentation and crosslinking among the ingredients. NVP has also a  $T_g$  value (175°C) that is higher than that (90°C) of TPGDA.  $T_g$  is a property that is related to the physical shape and geometrical arrangement of the molecule. The present report is aimed at focusing the effect of a codiluent on the properties of the films prepared with an oligomer, diluent and codiluent. The PH values of the properly cured films are, therefore, plotted (Fig. 2) against  $T_g$  values of the homopolymers of codiluents (EA, MA, CHA, VAc,

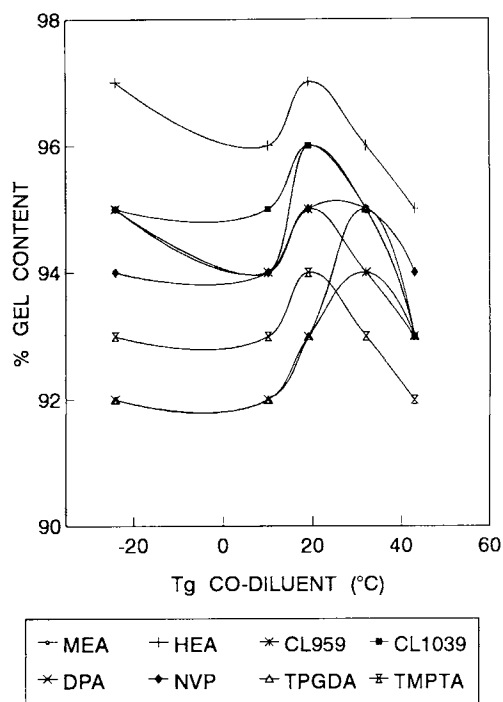


**Figure 2** Pendulum hardness is plotted against the glass transition temperature ( $T_g$ ) of codiluents in the UV system.

and t-BA). The PH values of the properly cured films are taken from Figure 1 and similar plots (not shown) of other codiluents (EA, MA, CHA, VAc, and t-BA). The  $T_g$  values of these codiluents are also taken from the literature.<sup>12</sup> It is quite interesting that there is a doping at around 20°C in each curve with variable extent of the doping. The reason of reduced hardness of each film at 20°C is not known at this stage, but similar unusual behavior was also observed by Kawate<sup>1</sup> and others<sup>2-4</sup> in the measurement of tensile properties of radiation-cured films of urethane acrylate.

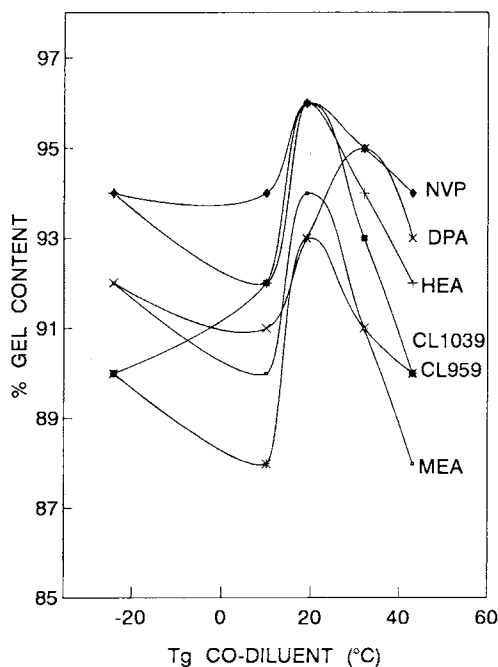
### Gel

Gel content determined by acetone solvent extraction of radiation-cured films is shown in Figure 3 (the UV-cured system) and Figure 4 (the EB-cured system) against  $T_g$  values of the codiluent. It is observed that most of the curves have registered a sharp rise in gel values at around  $T_g = 20^\circ\text{C}$ , irrespective of whether the radiation system is UV or EB. The only exception to this is with CL959 and NVP in UV and DPA with EB systems. It appears that the overall gel content is higher in the UV-cured systems than the EB-cured process. The relationship of gel content of the radiation cured films with  $T_g$  is important and is particularly interesting in the gel values having maxima at around 20°C and then it decreases. The gel content is a



**Figure 3** Gel content is plotted against the glass transition temperature ( $T_g$ ) of codiluents in the UV system.

representation of the overall crosslinking density in the cured films, while film hardness represents the crosslinking density at the surface of the cured film.

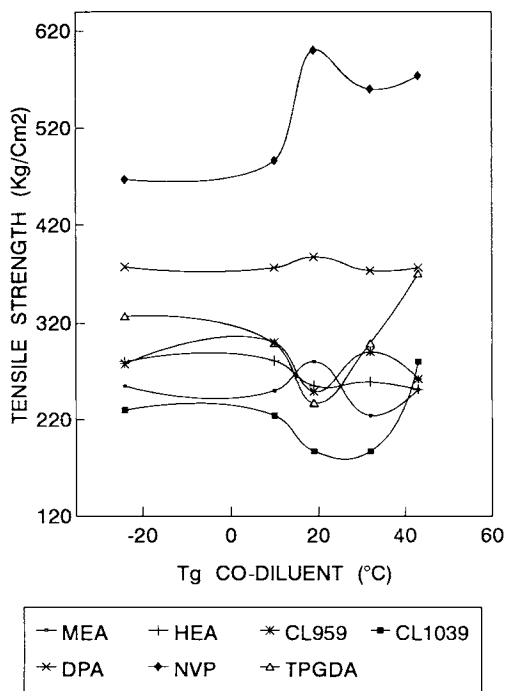


**Figure 4** Gel content is plotted against the glass transition temperature ( $T_g$ ) of codiluents in the EB system.

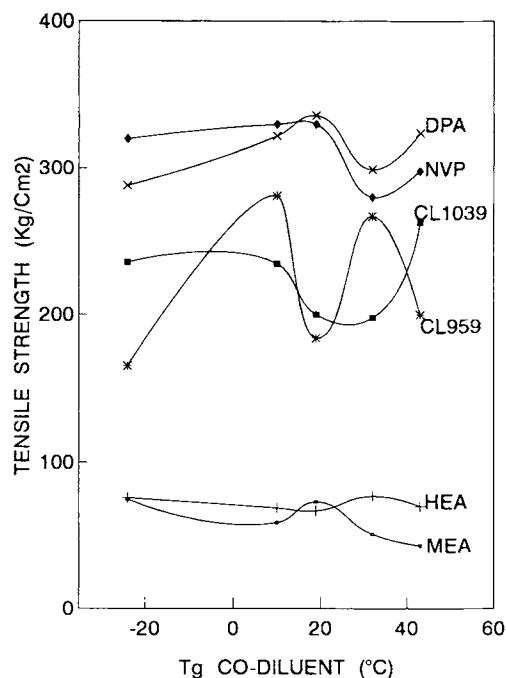
It is really interesting to note that the film hardness (Pendulum hardness, Fig. 2) decreases rapidly at around  $T_g = 20^\circ\text{C}$ , while there is a sharp increase of the gel content in Figures 3 and 4 at around the same  $T_g$  value ( $20^\circ\text{C}$ ). Perhaps ESR studies would spell out the real reasons of such contrasting phenomena as observed above (Figs. 2-4). Both short-lived and long-lived radiation-induced radical species could have been accounted for by the ESR studies. HEA series has produced the highest gel profile in the UV-cured system, and NVP, HEA, and CL1039 have exhibited the highest gel in the EB-cured system. This distinct difference in the UV and EB systems signifies the importance of adopting one radiation system over the other during selecting films of specific properties.

### Tensile Properties

Tensile strengths measured directly with INSTRON for the UV-cured and EB-cured films are plotted respectively in Figures 5 and 6 against  $T_g$  of the homopolymers of codiluent. NVP has produced the highest tensile strength (TS) in both the radiation systems, but the UV-cured film has much higher TS than that of the EB-cured polymer. DPA and NVP have almost similar TS values in the EB-cured sys-



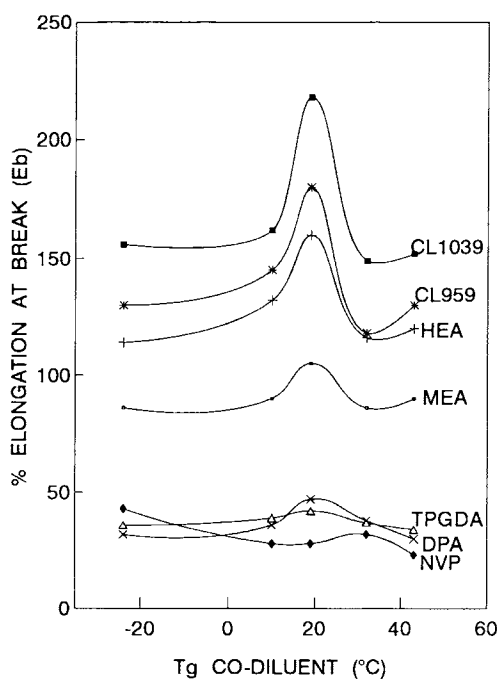
**Figure 5** Tensile strength of UV-cured films is plotted against the glass transition temperature ( $T_g$ ) of the homopolymer of the codiluent.



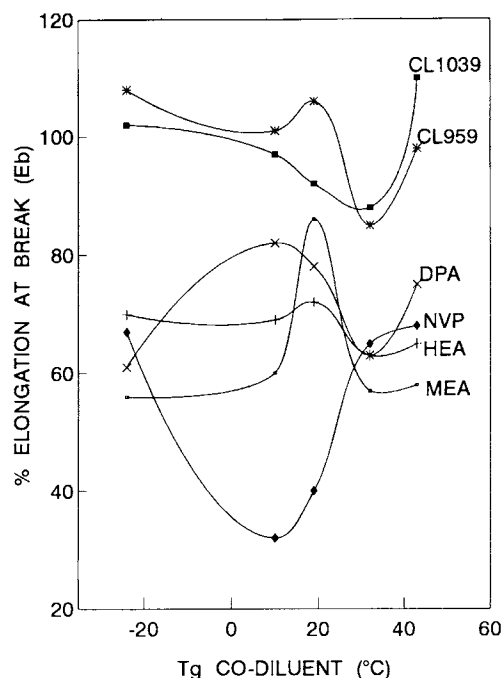
**Figure 6** Tensile strength of EB-cured films is plotted against the glass transition temperature ( $T_g$ ) of the homopolymer of the codiluent.

tem (Fig. 6); but the difference in TS values of UV-cured DPA and NVP series is quite significant (Fig. 5). The lowest TS value for the UV system is observed by the CL1039 series, whereas films of the HEA and MEA series have exhibited the lowest TS values in the EB system (Fig. 6). TMPTA films were so brittle in both the UV and EB radiation system that the films could not be properly peeled off the plates for tensile property measurements. TPGDA, being a difunctional diluent, should have produced the highest crosslinking leading to the highest TS values; but instead, NVP has produced the films of the highest strength. It is because NVP has the ability of better argumentation with the neighboring ingredients through the  $-\text{N}=\text{CO}-$  group present in NVP. The high difference of TS values of the UV-cured films over that of the EB-cured films illustrates a very significant importance of the UV radiation-cured film compared to the EB-cured polymers. The soft radiation by UV rays in the preparation of polymer modification has played a vital role in allowing the constituent ingredients to properly align their geometry in the line of attaining the maximum strength at the time of equilibrium conditions required during the polymerization process. The high energy electron beam has possibly disturbed this process to some extent, thereby reducing the overall tensile strength of the

produced polymer molecule. It is also interesting to note that some of the series like NVP, DPA, and MEA has registered maximum TS values at around  $T_g = 20^\circ\text{C}$  (Fig. 5) while others (TPGDA, CL1039, CL959, and HEA) have produced minimum TS values at this point ( $20^\circ\text{C}$ ). Similar is the case with the EB-cured system (Fig. 6). This contrasting behavior is also not clearly known at this point, but it may relate to the structural shape and geometry of the reacting ingredients of both diluent and codiluent present in the formulations. Surprisingly, elastic property of the UV-cured film denoted by elongation at break  $E_b$  is observed to be different in Figure 7, where  $E_b$  has been plotted against  $T_g$  of the codiluent. In this case, there is the maximum  $E_b$  value at  $T_g = 20^\circ\text{C}$  with all the series except NVP that has registered the lowest  $E_b$  value compared to the highest  $E_b$  exhibited by the CL1039 series. But the elastic behavior of EB-cured films of similar solutions is different in some respect, as observed in Figure 8, where the  $E_b$  of the EB-cured film is shown against  $T_g$  of the codiluent. The differential elastic behavior of the EB-cured films is observed between  $T_g$  values of 10 and  $30^\circ\text{C}$ , whereas this is very distinctly observed in the UV-cured system at  $T_g = 20^\circ\text{C}$ . This differential behavior of the EB-cured and UV-cured films of similar solutions is important for the diversified use of the polymers.



**Figure 7** Elongation at break of UV-cured films is plotted against the glass transition temperature ( $T_g$ ) of the homopolymer of the codiluent.



**Figure 8** Elongation at break of EB-cured films is plotted against the glass transition temperature ( $T_g$ ) of the homopolymer of the codiluent.

### Thermal Behavior

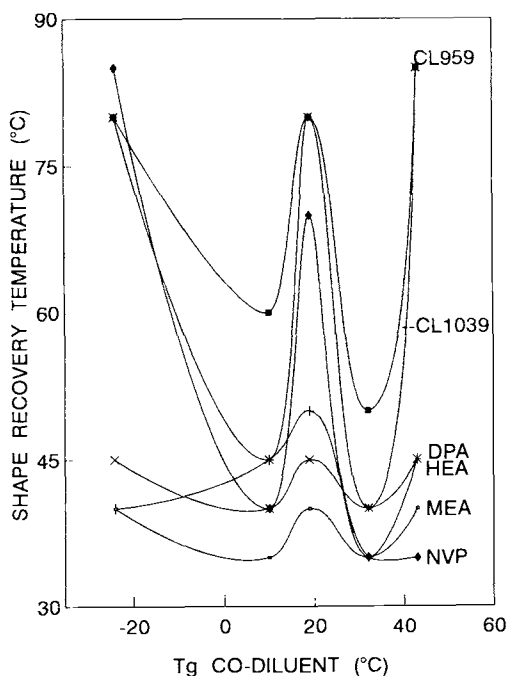
Polymer is a unique material that can be used in different weathering conditions in diversified applications if proper ingredients are present in the formulation. Some of the polymers can be thermally expanded and deformed in order to suit its applications as desired; but the deformed shape can be reverted to the original shape by heating the deformed polymer at different temperatures, depending on the nature and characteristic of the polymer. The polymer that remembers its original shape is called the shape memory polymer, and the temperature at which it can gain its initial shape is called the shape memory (recovery) temperature.

Fortunately, urethane diacrylate prepolymer has been able to prepare films with shape recovery (memory) character under EB and UV radiation in the presence of the monofunctional reactive diluents and codiluents studied in this investigation. The shape recovery temperature of the cure film is plotted against the  $T_g$  of the codiluent and is shown in Figure 9 (the UV system) and Figure 10 (the EB system). As the  $T_g$  value increases (from  $-24^\circ\text{C}$ ), the shape recovery temperature falls up to  $T_g = 10^\circ\text{C}$  and then suddenly increases at  $T_g = 20^\circ\text{C}$  and falls at  $T_g = 32^\circ\text{C}$  and rises again (Fig. 9). This behavior is more prominent with CL1039, CL959, and NVP

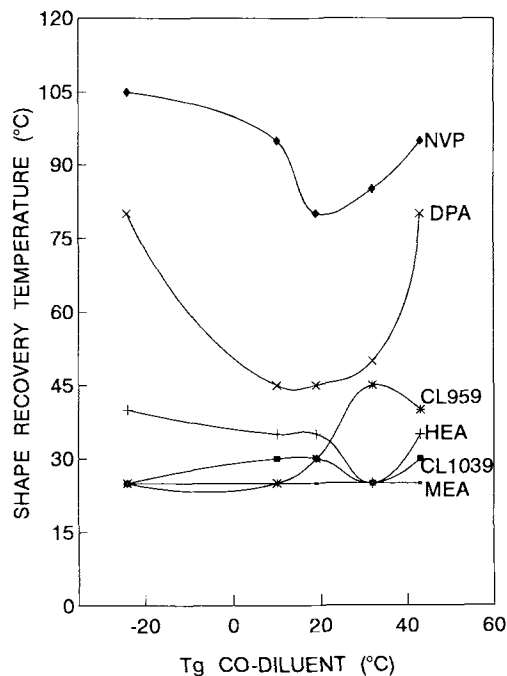
films. All the UV-cured films need heating above the ambient temperature of 25°C; but in the case of EB-cured films (Fig. 10), there are some films (MEA, CL1039, CL959, and HEA) that show shape recovery at temperatures below 30°C. The EB-cured films of NVP and DPA show shape recovery at relatively higher temperatures.

## CONCLUSIONS

Comparing different rheological properties of both EB-cured and UV-cured films of urethane diacrylate, it appears that the UV-cured films possess uniform order in the determination of its various properties; UV-cured films contain much higher TS and Eb values than the EB-cured films of the similar formulations. The shape recovery temperatures of the UV-cured films are also more defined than that of the EB-cured polymer. It can, therefore, be said that UV curing, in some cases, is much more beneficial; moreover, the cost of UV curing system is much less than that of the EB process.



**Figure 9** Shape recovery temperature of UV-cured films is plotted against the glass transition temperature ( $T_g$ ) of the homopolymer of the codiluent.



**Figure 10** Shape recovery temperature of EB-cured films is plotted against the glass transition temperature ( $T_g$ ) of the homopolymer of the codiluent.

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