

Interactive effects of resin composition and ambient temperature of light curing on the percentage conversion, molar heat of cure and hardness of dental composite resins

J. VAIDYANATHAN, T. K. VAIDYANATHAN

New Jersey Dental School, University of Medicine and Dentistry of New Jersey, 110 Bergen Street, Newark, NJ 07103-2425, USA

The interactive effects of ambient temperature of cure and resin composition on the extent of cure are evaluated by the measurement of percentage conversion of double bonds, heat of cure and microhardness of visible light cure dental resin systems. Three bonding agents, including two BisGMA-based resins (Command Bond, Pentron Bond) and one urethane-dimethacrylate-based resin (Coe Bond), were evaluated. The results indicate a significant effect of ambient temperature of cure and resin composition on percentage conversion, molar heat of cure and microhardness. In the temperature range of 25–60 °C, thermal activation appears to be a promising approach to improve conversion and crosslinking in dental resins. At lower ambient temperatures of cure (25 °C), urethane dimethacrylate resin undergoes higher levels of conversion than BisGMA-based resins. At higher temperatures, the percentage conversion increases with temperature in all resins. However, the molar heat of cure and hardness values show a significant increase with temperature only in BisGMA-based resins, but not in the urethane dimethacrylate resin. The difference in percentage conversion and heat of cure variation with temperature and the similarity of the latter variation with that of microhardness, probably indicates that the heat of cure is a better predictor of the extent of cure in these thermoset resins. It appears that enhanced crosslinking due to thermal activation may significantly influence the extent of cure at higher ambient temperatures.

Introduction

The adverse effects of unreacted methacrylate groups in polymeric materials have been widely documented in the literature. Grassie [1] had originally linked the hydrolytic and other environmental degradation of polymers with the presence of reactive double bonds. Soderholm *et al.* [2, 3] and Wu *et al.* [4] attributed *in vivo* wear processes and subsurface porosity of composite restorations to hydrolytic degradation and environmental softening, respectively. Erosion, accelerated ageing, filler debonding, wear, chemical attacks and other degradation processes involving dental composites have been attributed to the reactivity of the unreacted methacrylate groups by several authors [5–9]. Ruyter *et al.* [10], Asmussen [11], Ferracane [12, 13] and Antonucci *et al.* [14] have reported that 25 to 55% reactive double bonds may be retained in the cured dental composite resins. The presence of such large amounts of unreacted methacrylate groups cause not only environmental degradation of the composite resins but also adverse effects on their physical and mechanical properties [12, 13, 15, 16]. There is therefore a consensus that improved conversion of double bonds is critical in the optimization of the stability, durability and physico-mechan-

ical properties of dental composites. There is also growing evidence that improved conversion can be accomplished by postcure thermal processing [17, 18] and control of ambient temperature of curing by preheating the raw paste [19–23]. The objectives of this investigation were to evaluate by infrared, thermal analysis and microhardness methods the interactive effects of resin composition and ambient temperature of cure on the percentage conversion, molar heat of cure and hardness of selected visible light cure commercial unfilled resins (bonding agents).

Materials and methods

Three commercial dental resin systems were studied in this investigation. These included a urethane-dimethacrylate-based resin (Coe Bond from ICI) and two BisGMA-based resins (Command Bond from Kerr and Light Cure Bond from Pentron). Table I lists the composition of the resins. All of these resins are commercial bonding agents with no filler. Percentage conversion, heat of cure and hardness values were determined as a function of ambient temperature of cure by the following methods.

TABLE I Resins, compositions and manufacturers

S. no.	Resin brand	Manufacturer	Composition
1	Command Bond	Kerr, Michigan	75% BisGMA ^a 25% TEGDMA ^b
2	Pentron Bond	Pentron Inc., CT	60% BisGMA 40% TEGDMA
3	Coe Bond	ICI, UK	50% UEDMA ^c 50% TEGDMA

^a BisGMA, Bisphenol glycidyl methacrylate.

^b TEGDMA, Triethylene glycol dimethacrylate.

^c UEDMA, Urethane dimethacrylate.

Procedure for the determination of percentage conversion

Transparent KBr discs were prepared and used as windows for polymer and monomer films. A small drop of the unfilled resin was placed between two KBr discs, pressed into a film and was scanned to get the infrared (IR) spectrum. After the IR spectral scan, the monomer films between the discs were cured (after equilibration for 15 min inside a specially fabricated heating chamber maintained at 25, 40 or 60 °C, respectively) by light exposure on each side of the film for 20 s with an ESPE Elipar light source (Premier). The polymer films thus obtained were again scanned for the FTIR spectrum. Fig. 1A, B is an illustration of the FTIR spectra before and after polymerization. The percentage conversion calculation followed the method by other authors [10–13] and used the relationship, percentage conversion = 100 – R, where

$$R = \frac{(A \text{ at } 1636 \text{ cm}^{-1}) / (A \text{ at } 1610 \text{ cm}^{-1} \text{ (polymer)})}{(A \text{ at } 1636 \text{ cm}^{-1}) / (A \text{ at } 1610 \text{ cm}^{-1} \text{ (monomer)})}$$

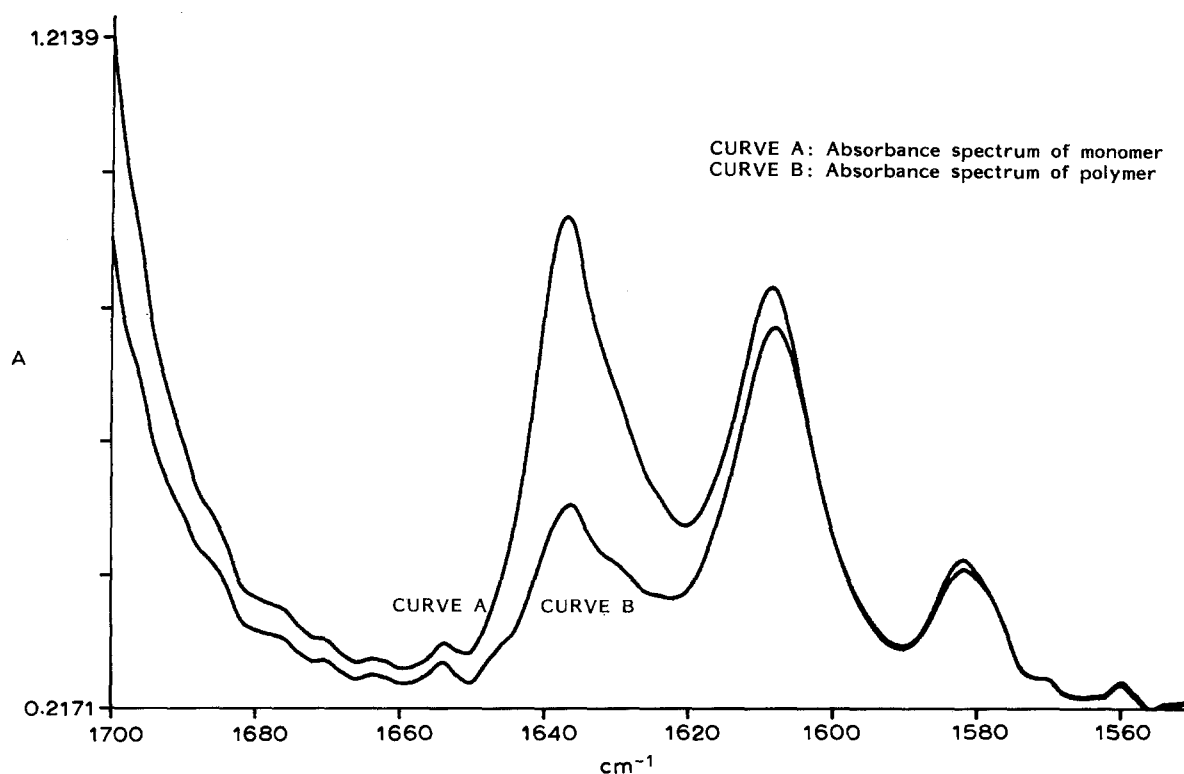


Figure 1 Fourier transform infrared spectra of monomer and polymer films.

where A is absorbance. A Perkin-Elmer FTIR model 1600 was used in the study.

Procedure for the determination of heat of cure

The heat of cure was determined with a du Pont differential scanning calorimeter (DSC) interfaced to a computer data station, du Pont Thermal Analyst 2000. 15–20 mg samples of the resin were placed in the sample pan of the DSC cell, held isothermally at 25, 40 or 60 °C, respectively. The resins were cured by 20 s exposure with Elipar light. During the light curing, the light probe was mounted on a stand. The cell cover was removed and the light probe positioned at the same height as the cell cover, following previously marked positions on the stand to standardize the probe height. Both the sample pan and the reference pans were simultaneously exposed to the light to determine the exotherm due to the overall heat output. Light exposure was repeated (with the sample pan containing the cured sample) to determine the exotherm corresponding to the baseline heat output due to the light source only. Fig. 2 shows a typical exotherm in Coe Bond and also illustrates the heat of cure calculation. The difference between the overall heat output (first exotherm) and the average of two successive baseline heat outputs (second and third exotherms) was determined as the heat of cure of the resin. From the heat of cure values, the molar heat of cure was calculated using the compositions in Table I and the molecular masses of 968, 512 and 286 for urethane dimethacrylate in Coe Bond, BisGMA and TEGDMA, respectively [24].

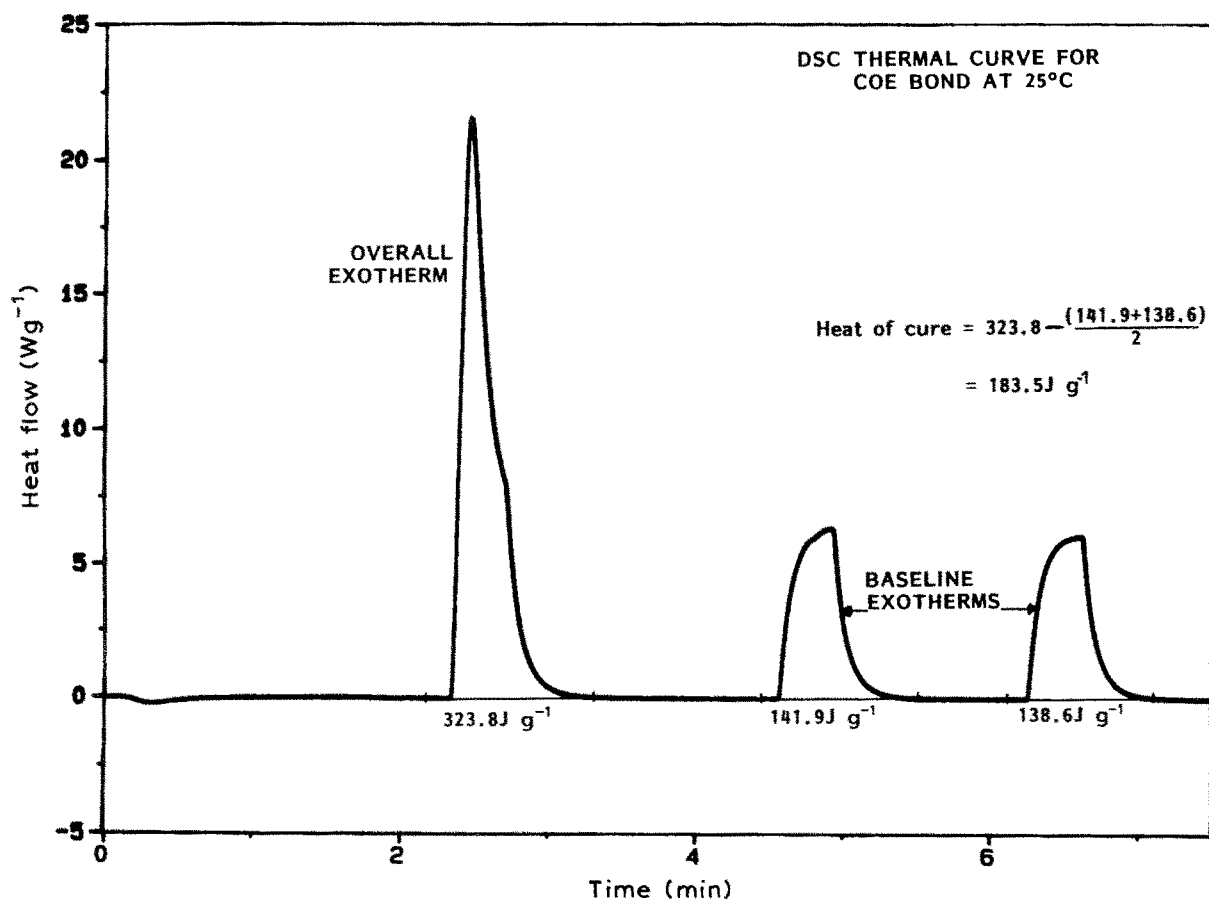


Figure 2 DSC thermal curve for Coe Bond at 25°C. The illustration of heat of cure calculation is based on subtraction of the average of the baseline exotherms from the overall exotherm. The integrated area of the exotherms is used for the calculation.

Hardness measurement

Hardness was measured on disc samples (6 mm × 3 mm thick). The discs were prepared by condensing the resin in split stainless steel ring moulds. The samples were clamped between glass slides, transferred to the heating chamber, held isothermally at 25, 40 or 60°C, equilibrated for 15 min to preheat the paste to the chamber temperature and cured by light exposure from the top for 40 s in the chamber. After the cure, the disc samples were separated from the mould and the hardness measured in a Wilson microhardness tester, using a load of 200 gm. Top and bottom hardness were determined using a Knoop indenter. All hardness measurements were carried out within 15 min after light activated cure.

The percentage conversion, molar heat of cure and hardness data obtained were statistically analysed by two-way ANOVA involving temperature and composition variables followed by Duncan's multiple range tests. Correlation coefficient matrices between different variables were also calculated. The above statistical analysis used the SAS statistical program.

Results

Figs 3 and 4 show the variations of percentage conversion and molar heat of cure as a function of resin brand and ambient temperature of cure. Figs 5 and 6 show the bar graphs showing the corresponding variations of top and bottom hardness. The role of resin composition and temperature on different properties

appears significant. Two-way ANOVA of percentage conversion, molar heat of cure and hardness data revealed significant differences due to the main effects of resin composition and temperature as well as two-way interaction (resin-temperature) effects at $P < 0.001$ (see Table II). Duncan multiple range tests revealed homogeneous subsets in Tables IIIa, b, which also include the major resin-temperature interactive effects together with the homogeneous subsets formed from the pooled data for each variable. The results clearly indicate the following:

1. At room temperature, the urethane dimethacrylate resin (Coe Bond) has the highest percentage conversion, molar heat of cure and hardness compared with the corresponding mean values for the BisGMA-based resins.

2. With increasing ambient temperature during curing, the mean percentage conversion values are significantly higher as a function of temperature. This would indicate a potential for significantly improved conversion with higher ambient temperature of cure by preheating the composite paste.

3. The mean values of molar heat of cure and microhardness generally increase with increasing ambient temperature during curing. However, the urethane-dimethacrylate-based resin, Coe Bond shows no significant change in the molar heat of cure and surface hardness as a function of ambient temperature during curing.

Pearson correlation coefficient matrices were determined between different variables for individual resins

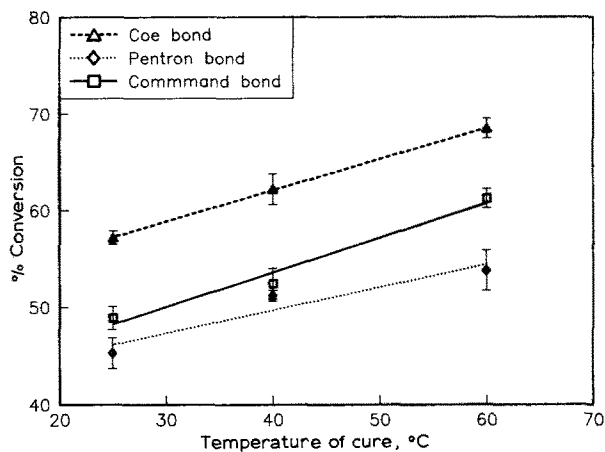


Figure 3 Variation of percentage conversion with temperature in different resins. Observe the linear regression fit. The coefficient of determination (R^2) values range from 0.91 for Pentron Bond to 1 for Coe Bond.

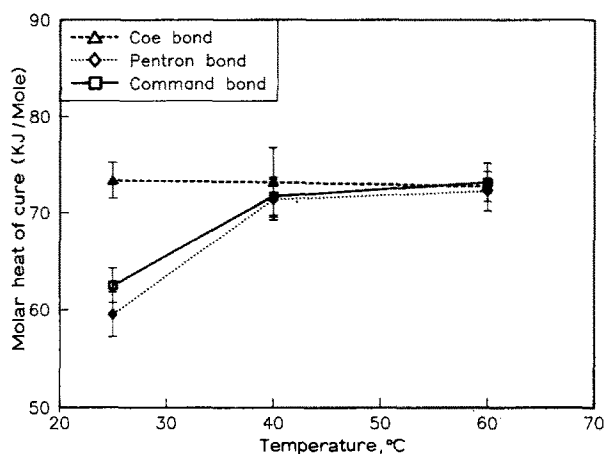


Figure 4 Molar heat of cure variation with temperature. Observe the significant increase of molar heat of cure between 25 and 40°C in Command and Pentron Bonds. Note the absence of increase of molar heat of cure values with temperature in Coe Bond.

and for pooled data of all resins. The variables considered included temperature, top hardness, bottom hardness, percentage conversion and molar heat of cure. Table IV gives the results when the data for all the resins were pooled in the correlation analysis. The values in the table include the Pearson correlation coefficient (R), the significance of correlation (P) and the total number of observations (N) used in the analysis. Significant association between all the variables are indicated except between temperature and top hardness. Table V lists the results of the correlation analysis for the individual resins separately. Observe that significant positive correlation ($P < 0.01$) between all pairs of variables are seen in BisGMA-based resins Command Bond and Pentron Bond. For the urethane-dimethacrylate-based Coe Bond, however, a significant level of positive correlation is observed only between temperature and percentage conversion. Other variables show either no significant correlation or only negative correlation at $P < 0.01$. Thus the correlation analysis clearly separates the temperature effect of molar heat of cure and hardness

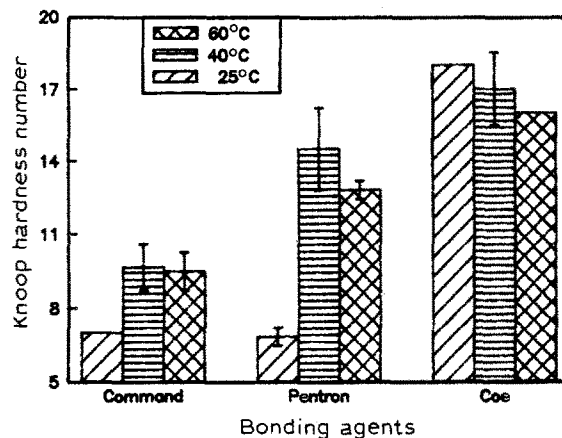


Figure 5 Bar graph of top hardness as a function of resin brand and Temperature. The absence of error bars in some bars (e.g. Coe Bond at 40°C and 60°C, Command Bond at 25°C) is due to lack of scatter in the experimental data.

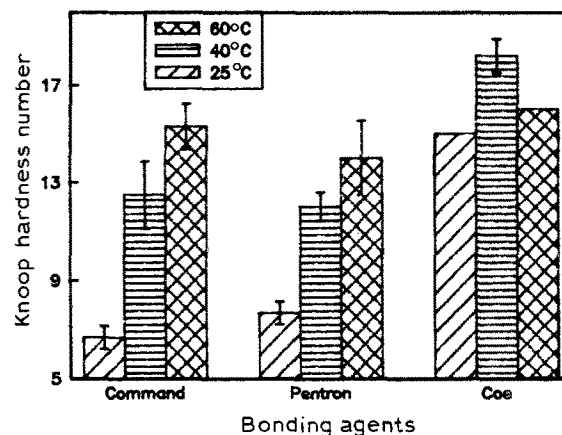


Figure 6 Bar graph of bottom hardness as a function of resin brands and temperature.

values of BisGMA-based resins and urethane-dimethacrylate-based resins, as indicated previously.

The above results clearly indicate strong interactive effects of resin composition and ambient temperature during visible light curing in determining the percentage conversion of double bonds, molar heat of cure, surface hardness and depth of cure of dental composite resin systems.

Discussion of results

The most significant observations in this investigation are the pronounced effects of resin composition and ambient temperature during light curing on important properties such as the percentage conversion of double bonds, molar heat of cure, surface hardness and depth of cure. Thus the increases as a function of temperature in the mean values of percentage conversion, molar heat of cure, top hardness and bottom hardness are as high as 20%, 21%, 85% and 115% respectively. The effect of thermal activation on the measured properties is remarkable. Proper choice of ambient temperature of cure and optimization of resin composition can be valuable methods to optimize composite properties for clinical use. In considering the selection of resin composition, the percentage

TABLE II Summary of two-way ANOVA results for percentage conversion, molar heat of cure, top hardness and bottom hardness data

S. no.	Dependent variable	Source (independent variables, interaction, error)	DF	Mean square	'F' ratio	P
1	% Conversion	Temperature	2	345	193	< 0.0001
		Brand	2	489	274	< 0.0001
		Interaction (temp. × brand)	4	49.9	5.6	< 0.0002
		Error	27	1.78	—	—
		Total	35	—	—	—
2	Molar heat of cure	Temperature	2	9.12	33.8	< 0.0001
		Brand	2	3.98	14.7	< 0.0002
		Interaction (temp. × brand)	4	2.66	9.9	< 0.0002
		Error	18	0.27	—	—
		Total	26	—	—	—
3	Top hardness	Temperature	2	45.8	49	< 0.0001
		Brand	2	321	344	< 0.0001
		Interaction (temp. × brand)	4	35.16	38	< 0.0001
		Error	45	0.933	—	—
		Total	53	—	—	—
4	Bottom hardness	Temperature	2	147	173	< 0.0001
		Brand	2	152	178	< 0.0001
		Interaction (temp. × brand)	4	24.4	28	< 0.0001
		Error	45	0.852	—	—
		Total	53	—	—	—

TABLE IIIa Homogeneous subsets of pooled data (Vertical connecting lines indicate homogeneous subset)

S. no.	Property type (units)	Variable	Specific variable	Property value	Remarks
1	Conversion (%)	Resin	Coe Bond	62.82	Pooled data
			Command Bond	58.28	
			Pentron Bond	50.11	
		Temperature (°C)	60	61.71	Pooled data
40	56.18				
25	51.01				
2	Heat of cure (kJ mol ⁻¹)	Resin	Coe Bond	76.10	Pooled data
			Pentron Bond	68.82	
			Command Bond	69.15	
		Temperature (°C)	60	73.21	Pooled data
		40	72.33		
		25	69.15		
3	Top hardness (KHN)	Resin	Coe Bond	17	Pooled data
			Pentron Bond	11	
			Command Bond	8	
		Temperature (°C)	60	13	Pooled data
		40	14		
		25	11		
4	Bottom hardness (KHN)	Resin	Coe Bond	16	Pooled data
			Pentron Bond	11	
			Command Bond	11	
		Temperature (°C)	60	15	Pooled data
		40	14		
		25	10		

conversion, molar heat of cure, top hardness and bottom hardness are highest at room temperature for the urethane dimethacrylate resin, Coe Bond. The BisGMA-based resins, Command Bond and Pentron Bond show lower percentage conversion, molar heat of cure, top hardness and bottom hardness, when cured at the ambient temperature of 25 °C. This difference between urethane dimethacrylate resin used in Coe Bond and the BisGMA-based Pentron and Command Bonds can be evaluated by an examination of

their molecular structures. Fig. 7 shows the reported molecular structure of the urethane dimethacrylate resin used in Coe Bond [24] and those of BisGMA and TEGDMA molecules. Two possible factors can be examined in considering the structural effects.

1. As pointed out by Ruyter [24], the flexibility of the urethane dimethacrylate molecule is probably higher than that of BisGMA because of a higher ratio of aliphatic chain length to the number of aromatic rings in the molecule.

TABLE IIIb Effect of temperature by brand on properties (homogeneous subsets) (Vertical connecting lines indicate homogenous subset)

S. no.	Property type	Temperature (°C)	Resin brand and property mean		
			Command Bond	Coe Bond	Pentron Bond
1	Molar heat of cure (kJ mol ⁻¹)	25	62.53	73.42	59.56
		40	71.78	73.84	71.41
		60	73.21	74.09	72.29
2	Conversion (%)	25	48.91	57.21	45.28
		40	52.46	62.18	51.21
		60	61.22	68.47	53.81
3	Top hardness (KHN)	25	7	18	7
		40	10	17	14
		60	10	16	13
4	Bottom hardness (KHN)	25	7	15	8
		40	13	18	12
		60	15	16	15

TABLE IV Pearson correlation coefficient matrix for all resins combined (Pearson correlation coefficient, *R*; probability, *P* (level of significance) and number of observations, *N*; in order)

	Temperature	Top hardness	Bottom hardness	% Conversion	Molar heat of cure
Temperature	1.000 0.0 54				
Top hardness	0.195 0.158 54	1.000 0.0 54			
Bottom hardness	0.570 0.0001 54	0.760 0.0001 54	1.000 0.0 54		
% Conversion	0.626 0.0001 36	0.656 0.0001 36	0.824 0.0001 36	1.000 0.0 36	
Molar heat of cure	0.570 0.0019 27	0.699 0.0001 27	0.805 0.0001 27	0.711 0.0001 27	1.000 0.0 27

2. The mobility of the BisGMA molecule is probably inhibited by the presence of hydrogen bonds due to two hydroxyl groups in its molecular structure. The presence of such hydrogen bonds may lead to bridging or association between molecules, thus resulting in reduced mobility.

Probably because of these structural effects, higher degree of cure is observed at room temperature (25 °C) in Coe Bond than in the BisGMA-based resins. The effects of thermal activation on percentage cure appears to be two-fold:

(a) Increased percentage conversion due to reduction of unreacted methacrylate groups at higher ambient temperature of cure.

(b) Enhanced crosslinking during cure at the higher temperature.

The results indicate that the percentage conversion increases with increasing temperature in all the resins investigated (see Fig. 3). However, the molar heat of cure increases with temperature only for the BisGMA-based resins and not for urethane-dimethacrylate-based Coe Bond, as indicated in Fig. 4. This difference in the variation of percentage conversion and molar heat of cure with temperature raises some interesting

questions. Antonucci *et al.* [14] have calculated percentage conversion values by DSC measurements of the heat of cure in BisGMA-TEGDMA resins. The basic assumption in the above work is that the total heat of cure is the sum of heat of conversion of participating vinyl groups. This assumption, although reasonable for linear and branched structures, may not be valid when significant crosslinking reactions occur. Since the heat produced in a crosslinking reaction may be influenced by steric, chemical and other energetic factors, the heat output due to a crosslinking reaction may not be identical to that of a simple opening up of a double bond. Manz and Creedon [25] have pointed out that while infrared measurement of percentage conversion is based on the disappearance of double bonds, the DSC measurement of heat of cure reflects the heat output produced by both the opening up of double bonds and crosslinking reactions. It is therefore the opinion of the authors that the difference in the variation of percentage conversion and molar heat of cure with temperature and the similarity of the latter variation to that of surface hardness with temperature, is an indication that molar heat of cure is a better predictor of the extent of cure in thermoset

TABLE V Pearson correlation coefficient matrix for each individual resins (Pearson correlation coefficient, R ; probability, P (level of significance) and number of observations, N ; in order)

S. no.	Resin	Variable	Variable Temperature	Top hardness	Bottom hardness	% Conversion	Molar heat of cure
1	Command Bond	Temperature	1.000 0.0 18				
		Top hardness	0.684 0.0017 18	1.000 0.0 18			
		Bottom hardness	0.926 0.0001 18	0.817 0.0001 18	1.000 0.0 18		
		% Conversion	0.965 0.0001 12	0.717 0.0087 12	0.835 0.0007 12	1.000 0.0 12	
		Molar heat of cure	0.841 0.0045 9	0.854 0.0034 9	0.831 0.0055 9	0.807 0.0086 9	1.000 0.0 9
2	Pentron Bond	Temperature	1.0000 0.0 18				
		Top hardness	0.655 0.0032 18	1.000 0.0 18			
		Bottom hardness	0.898 0.0001 18	0.796 0.0001 18	1.0000 0.0 18		
		% Conversion	0.893 0.0001 12	0.808 0.0015 12	0.876 0.0002 12	1.0000 0.0 12	
		Molar heat of cure	0.819 0.0069 9	0.960 0.0001 9	0.858 0.0031 9	0.942 0.0001 9	1.000 0.0 9
3	Coe Bond	Temperature	1.000 0.0 18				
		Top hardness	-0.677 0.0020 18	1.0000 0.0 18			
		Bottom hardness	0.220 0.3805 18	-0.167 0.5065 18	1.0000 0.0 18		
		% Conversion	0.978 0.0001 12	-0.878 0.0002 12	0.231 0.4709 12	1.0000 0.0 12	
		Molar heat of cure	-0.139 0.7218 9	0.135 0.7298 9	-0.287 0.4544 9	-0.043 0.9121 9	1.000 0.0 9

resins studied in this investigation. In other words, there is a need to distinguish between polymer chain lengthening and crosslinking reactions in thermoset resins. Bausch *et al.* [26] studied the effect of elevated temperature on the mechanical properties of chemically activated dental composites and reported significant improvement of selected properties with increasing temperature. They also interpreted their results as indicative of increased crosslinking at higher temperatures of cure. The results of our study and those of Bausch *et al.* indicate that crosslinking is a higher energy process favoured at higher temperatures, both in the chemical cure systems as well as the photocure systems. Based on this premise, the interpretation of our data is straightforward. Thus, assuming that crosslinking increases with molecular flexibility and mobility, the higher molar heat of cure of the Coe Bond at the lower ambient temperature of cure

(25 °C) is an indication of a higher degree of crosslinking. Because of the higher molecular mobility and flexibility even at 25 °C, the energy for enhanced crosslinking is probably available in this system at this temperature. The higher hardness values of the Coe Bond as a result of light cure at 25 °C also support this interpretation. With increasing ambient temperature of cure, however, no significant increase in the molar heat of cure and the hardness values is observed in the Coe Bond, probably suggesting that no significant additional crosslinking occurs. However, some additional conversion of vinyl groups is indicated by the percentage conversion measured by FTIR. In the BisGMA-based resins of Command and Pentron Bonds, the lower molar heat of cure and hardness values observed at lower ambient temperature of cure (25 °C) probably indicate a lower degree of crosslinking. With increasing ambient temperature of cure,

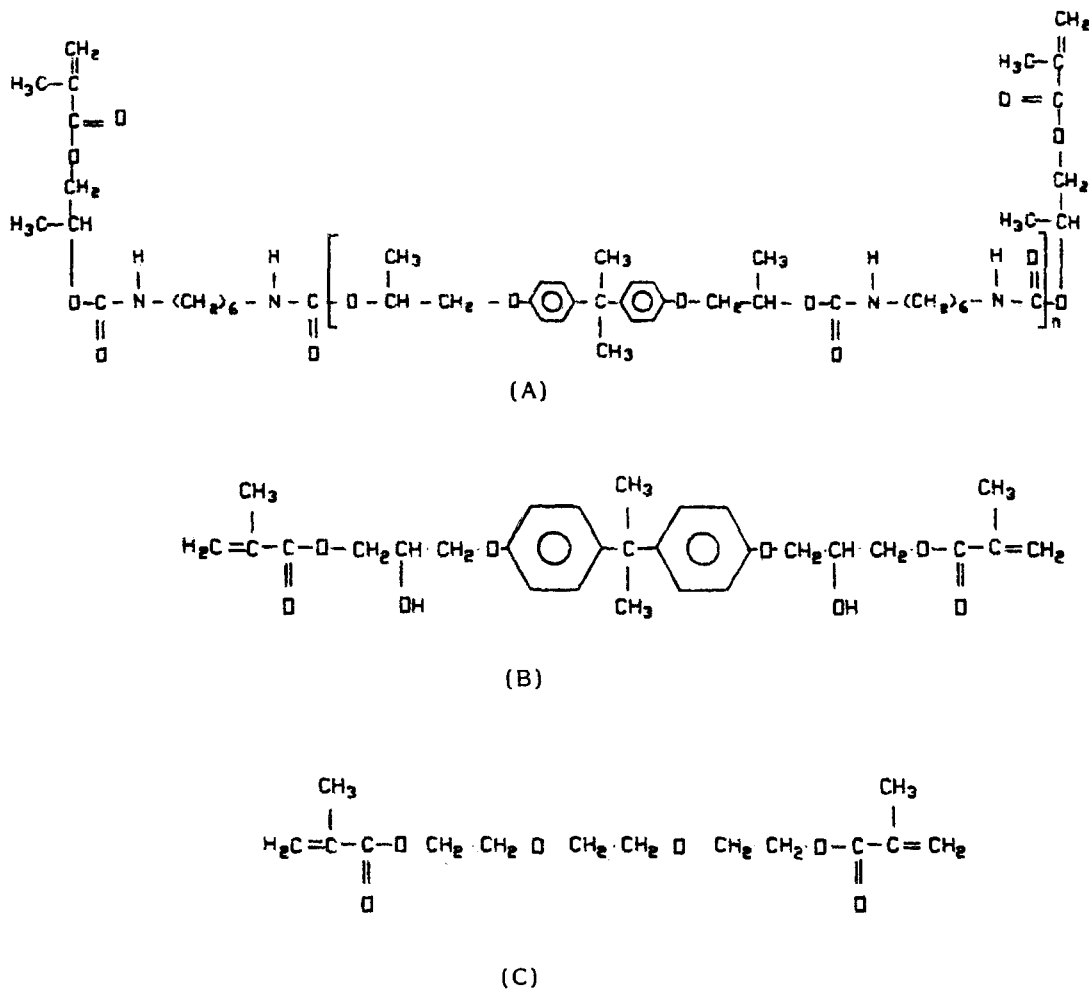


Figure 7 Molecular structures of different resins: (a) urethane dimethacrylate used in Coe Bond; (b) BisGMA; (c) TEGDMA.

crosslinking may be enhanced by thermal activation, leading to higher molar heat of cure and hardness values. Thermal activation may increase the flexibility and the mobility of the molecular chains through reduction or elimination of molecular bridging and association, leading to enhanced crosslinking and cure. The effects of thermal activation appears to be more pronounced in the 25–40 °C temperature range (see Fig. 4). From a clinical point of view, this indicates that preheating the composite paste to 40 °C before placement in the oral cavity may improve conversion and cure during photopolymerization. The use of composites directly from the refrigerator shelf to the oral cavity is certainly contra-indicated by the results of this study. Such practice may lead to poorer conversion and cure, possibly leading to premature failure of the restoration.

The results of this study also suggest that enhanced values of molar heat of cure, hardness and changes in other properties may be influenced by the degree of crosslinking in the resins investigated. Percentage conversion values measured in FTIR may not always reflect the extent of cure in thermoset resins, where crosslinking reactions contribute to the curing processes.

Conclusions

The results of this study have indicated the interactive

effects of resin formulation and ambient temperature of cure on the percentage conversion, molar heat of cure, surface hardness and depth of cure of selected bonding agents. With increasing ambient temperature of cure, the percentage conversion increases in all resins. The molar heat of cure and surface hardness increase with temperature only in the BisGMA-based resins studied. In the urethane dimethacrylate resin, heat of cure and hardness are high even during room temperature curing and no significant increase in these quantities is observed as a function of ambient temperature of cure. These results may be related to the presence of hydrogen bond in BisGMA systems and the enhanced mobility of the reactive groups induced by thermal activation. The absence of hydrogen bond in urethane dimethacrylate and its greater molecular flexibility account for the relatively higher percentage cure or crosslinking by room temperature curing of the Coe Bond. The absence of thermal activation on crosslinking reactions in this resin may also be associated with the above factors.

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