RESEARCH ARTICLE

Amorphous Macromers as Potential Organic Matrix in Dental Composites

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ABSTRACT

Objectives: Assess the thermal and hydrolytic stability of patented macromer-based dental polymer matrices and composites

Methods: Polymer matrices and composites based on a patented material (IP:343192) containing hybrid amorphous macromers co-polymerized with one of the 4 different dimethacrylates was prepared and the thermal and photo-thermal behavior were assessed. Diffusivity resistance and cross-link density of polymers were assessed. Sorption ($S(t)$, $Mg\%(t)$ A $S\%(t)$ and solubility ($SL(t)$ A $SL\%(t)$) of composites in chloroform (CHCl3), tetrahydrofuran (THF), carbon tetrachloride (CCL) and acetone (Ace) for varying durations (1h, 24h 1mo), and deionized water for 120h were determined.

Results: Dual T$_g$ were noticed for both the matrices and composites; matrices containing BisGMA (G) and UDMA (U) as the dimethacrylate co-polymer showed significantly lower $SL(t)$. Matrix containing TEGDMA (T) as the dimethacrylate co-polymer showed the least $S(t)$. Matrix containing BisEMA (E) had the highest cross-link density. photo-DSC of composites showed a Degree of Conversion of 97% at lower enthalpies (15-28J/g). None of the composites showed water solubility. All materials showed solubility in acetone with U being the least. Sorption and solubility in other organic solvents was lower and occurred only at longer immersion time.

Conclusions: Amorphous hybrid macromer-based polymer matrices and composites show promising thermal and hydrolytic behavior.

Keywords: dental composite, macromer, thermal stability, glass transition, hydrolytic stability, cross-link density

Introduction

Dental composites are by far the widely used restorative materials. Composites have many attributes like being the only restorative material that is amenable for both direct and indirect procedures, besides being aesthetic, conservative and reasonably durable. Hydrolytic and thermal stability are utmost important for all restorations to withstand the rigors of oral environment. Different resin matrices with hydrophobic properties have been tried in the past to impart durability in oral environment. Notable among them are polycarbonates, polyurethanes and siloranes. Commercial composites using these resin types have proven to be successful in hydrolytic stability in oral environment. However, certain long-term drawbacks have been found with them. Macromers are fairly large resin molecules, with polymerizable end groups, imparting favorable properties of stability, conversion and lower shrinkage. This is primarily owing to their very high molecular weight and molar volume. Crystalline macromers of silicones with suitable terminal functional groups have been adapted for dental composite matrix application as they possess excellent hydrophobic property. As low as 2-10% incorporation of one such resin polyhedral oligomeric silsequioxane (POSS) imparts good flexural strength and modulus[1]. Single silicone polymers are being used in dental composite with reasonable success as either good biocompatible or low shrinking materials. Siloranes utilize ring-opening polymerization instead of the conventional free-radical polymerization of conventional resin based materials[2–7]. However, hybridizing two amorphous macromers of silicones with suitable terminal groups has not been tried so far. Such hybridization, could circumvent the disadvantages of one macromer and help get the best out of both the macromers in a balanced manner. The possibilities of tailor-making many such combinations, also opens the horizon for newer materials with superior properties than either of them alone. A new patented composite[8] has been developed, based on this principle. Four such organic resin matrices and composites with the hybridized macromers and one of the four dimethacrylates, namely urethane dimethacrylate UDMA (U), or ethoxylated bisphenol A glycidyl dimethacrylate BisEMA (E), or bisphenol A diglycidyl methacrylate BisGMA (G), or triethylene glycol dimethacrylate TEGDMA (T) were co-polymerized and quartz as filler was added for composites.

The aim of this study is to assess the thermal and hydrolytic stability of the new materials.

Materials and Methods

A representative ring-opening polymerizable silicone macromer used in the experimental material is given below (Fig 1). A representative free-radical polymerizable silicone macromer used in the experimental material is given below (Fig 2). A representative dimethacrylate used in the experimentalmaterial is given below (Fig 3).
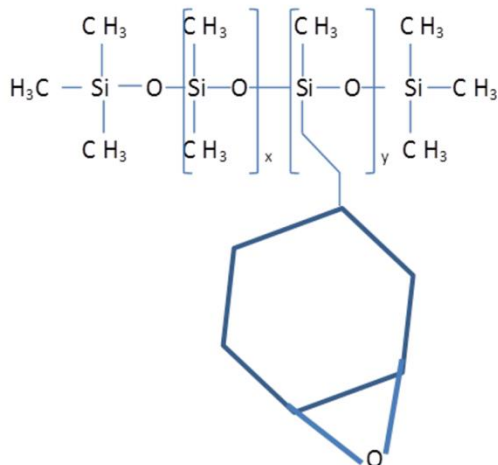

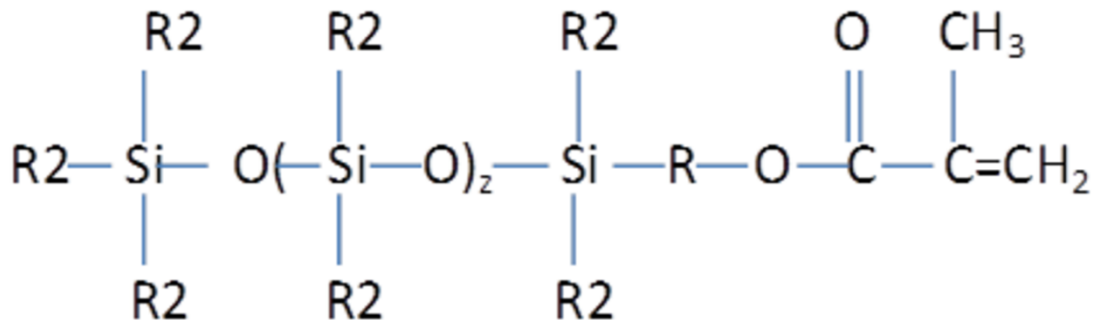Fig. 1: Representative cationic ring opening polymerizable macromer

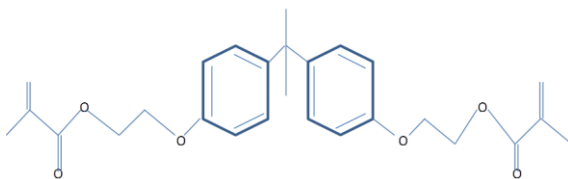Fig. 2: Representative free-radical polymerizable macromer

Fig. 3: Representative Dimethacrylate

Experiments on matrices

THERMAL ANALYSIS

Thermo-gravimetric Analysis (TGA) and Differential Scanning Calorimetric analysis (DSC) were done for the polymerized organic matrices to understand their thermal behavior. On a 5mm thick glass slab customized hollow cylinders (internal diameter - 5mm and height- 2mm) of High Density Poly Ethylene (HDPE) were stabilized with adhesive tapes to serve as moulds for sample preparation. The four experimental matrices (U, E, G and T) were filled in to the moulds and polymerized using a Quartz-Tungsten-Halogen (QTH) lamp at an average intensity of $740mW/cm^2$ for 40s after covering the surface with a 2mm thick microscopic cover slip. The samples were removed and the excess trimmed away with scissors.

Thermo-gravimetric Analysis (TGA): The sample of each group was mounted on the TGA platform (TA instruments) and the analysis wascarried out from room temperature to 1000^0 C.

Differential Scanning Calorimetric analysis (DSC): The sample material of each group was placed in the Aluminium crucible in the Differential Scanning Calorimeter (TA instruments) and the analysis was carried out in liquid Nitrogen from 0^0 C to 170^0 C, both heating and cooling at a rate of 20^0 C/min.

DETERMINATION OF HYDROLYTIC STABILITY AND DIFFUSIVITY RESISTANCE

Customized HDPE moulds (4mm internal diameter and 2mm height) stabilized on glass slab with adhesive tapes were used to prepare the samples of the four experimental matrices (U, E, G and T). A QTH lamp was used to activate the polymerization after the resin increments were placed in the moulds and the top surfaces covered with microscopic cover slip. The curing was done from the top surface only for 40s at an average intensity of $740mW/cm^2$. The excess was removed with a scalpel and the samples retrieved and their weights measured in an analytical calibrated electronic balance (Shimadzu Corporation, Kyoto, Japan) with an accuracy of ±0.01mg. The diameter and thickness of the specimens were measured using a digital Screw gauge cum micrometer Digimatic micrometer (Mitutoyo Corporation, Kanagawa, Japan) with a measuring range of 0-1" and resolution of 0.00001". The specimen thickness was measured from six points (5 in the perimeter and one in the centre) and the average was noted down. Any adsorbed moisture was removed by placing them in a desiccator containing CaCl2 under vacuum for 1h and heating

in an oven at 37^0 C for 2h under vacuum. The weights were measured again and considered as the pre-immersion weights ($m1$).

Equilibrium swelling: The samples were stored in 1mL of Tetra hydro furan (THF) in glass vials for 120h. The solvent was discarded and freshly added every day. After aging, the samples were dried in paper towel. The weights of the resin samples were measured ($m2$). The samples were placed in a desiccator containing CaCl2 under vacuum for 2h to remove the absorbed solvent. Further the samples were heated to 37^0 C under vacuum for 21h and the weights measured again ($m3$). Sorption and solubility were measured according to the following formulae:

$$S(t) = \frac{m2(t) - m3(t)}{V} \qquad \text{...Eq 1}$$

$$SL(t) = \frac{m1 - m3}{V} \qquad \text{...Eq 2}$$

$$Mg\%(t) = \frac{m2 - m1}{m1} * 100 \qquad \text{...Eq 3}$$

$$SL\%(t) = \frac{m1 - m3}{m3} * 100 \qquad \text{...Eq 4}$$

$$S\%(t) = Mg\% + SL\%(t) \qquad \text{...Eq 5}$$

Where, $m1$ is the initial dry weight of the specimen before aging in the solvent; $m2(t)$ is the weight (specimen + absorbed solvent) of the specimen after aging at a given time (t); $m3(t)$ is the dry, solvent-evaporated weight of the specimen obtained finally after thorough desiccation and drying in vacuum under heat; V is the volume of the specimen; $S(t)$ is the sorption at specific time (t); $SL(t)$ is the solubility at specific time(t); $Mg\%(t)$ is the percent apparent weight of sorbed solvent in the specimen at specific time(t) which excludes the amount of leached substances from the specimen during aging, that would have resulted in some weight loss; $SL\%(t)$ is the percent apparent solubility during aging at specific time(t) which excludes the amount of sorbed solvent that would have resulted in some weight gain; $S\%(t)$ is the actual percent of total sorbed substances at specific time (t).

Determination of Cross-link Density: After the equilibrium swelling in THF for 120h, the crosslink density of the experimental polymerized matrices was assessed using the following formula;

$$V_e = \frac{1}{M_c} \qquad \text{....Eq.6}$$

Where, v_e is the cross-link density and M_c is the weight of the sample between two elastically effective cross-links. It is the reciprocal of v_e. M_c is calculated by the following equation

$$M_c = \frac{v_1 \rho_2^{\frac{3}{2}} \sqrt{v_{2m} - \frac{v_{2m}}{2}}}{-\ln(1 - v_{2m}) + V_{2m} + \chi_{12} v_{2m}^2} \qquad \text{... Eq.7}$$

Where, V_1 is the molar volume of solvent; ρ_2 is the initial mass density of the polymer; V_{2m} is the molar volume of the equilibrium swollen polymer; X_{12} is the Flory-Huggins' polymer-solvent interaction parameter (Billmeyer Jr. 1994). The molar volume of equilibrium swollen polymer V_{2m} is calculated as

$$V_{2m} = \frac{W_0}{V_{equil}\rho_2} \qquad \text{...Eq. 8]}$$

Where, W0 is the initial weight of the polymer before swelling; V_{equil} is the equilibrium molar volume of the polymer, which is calculated by

$$v_{equil} = \frac{w_0}{\rho_2} + \frac{w_S - w_o}{\rho_1} \qquad \text{....Eq.9}$$

Where, w_S is the swollen polymer weight; ρ_1 is the mass density of the solvent.

Experiments on composites:

Thermal Analysis:
photo-DSC and DSC of the experimental composites was measured using Photo-DSC 204 *F1 Phoenix* (NETZSCH, Thermal Analysis of the NETZSCH Applications Laboratory, NETZSCH-Gerätebau GmbH, Wittelsbacherstr, Selb/ Bavaria, Germany).

For photo-DSC, samples of the four experimental composites weighing 9.75mg ($\pm$0.13) were placed on the Al crucible without lid for investigation of the curing behavior under UV exposure. The following parameters weremaintained: 40min isotherm at 35^0 C with UV curing unit (320 to 500 nm and exposure time of 10 seconds eachfor 8 irradiations once in every 5min at an intensity of $1W/cm^2$). Alternative cooling options such as fast liquid nitrogen (-180°C), gaseous phase of liquid nitrogen for smoothest cooling curves (-110°C), intracooler (-85°C) compressor cooling (RT) as well as accurate gas flows by three mass flow controllers (MFC) for two purge gases and one protective gas were the additional parameters for recording the calorimetry. Tau-Sensor was used to acquire the signal.

For DSC, samples of the four experimental composites weighing 11mg ($\pm$0.87) were placed on the Al crucible with perforated lid. The temperature program was as follows: -100^0 C …80^0 C….-100^0 C….80^0 C; heating/cooling rate was 10K/min in a Nitrogen atmosphere. Tau-Sensor was used to acquire the signal.

Instrument control and data acquisition were accomplished via a MS-Windows software and electronics system.Data evaluation was carried out by a comprehensive PC software package, allowing computation of peak and onset temperatures, inflection points, partial area integration, specific heat and transformation energetics.

DETERMINATION OF HYDROLYTIC STABILITY, SORPTION AND SOLUBILITY OF COMPOSITES IN ORGANIC SOLVENTS

Sample preparation was done similar to that of polymer matrix samples described under "*Experiment on matrices*" section. Weights of the samples were measured in an analytical calibrated electronic balance (Shimadzu Corporation, Kyoto, Japan) with an accuracy of $\pm$0.01mg. Any adsorbed moisture was removed by placing them in a desiccator containing $CaCl_2$ under vacuum for 1h and heating in an oven at 37^0 C for 2h under vacuum. The weights were measured again and considered as the pre-immersion weights ($m1$). The samples were stored in 1mL of deionized water or respective organic solvents THF, chloroform ($CHCl_3$), carbon tetrachloride (CCl_4) and Acetone in glass vials.

Hydrolytic Stability: The water was discarded and replenished freshly every day. After aging for 120h, the samples were dried in paper towel. The weights of the composite samples were measured ($m2$). The samples were placed in a desiccator containing $CaCl_2$ under vacuum for 2h to remove the absorbed water. Further the samples were heated to 37^0 C under vacuum for 21h and the weights measured again ($m3$).

Sorption and Solubility in organic solvents: The composites were aged in the four organic solvents for 3 durations, 1h, 24h and 1 month. The solvent was discarded and replenished freshly every day for the 1 month sub-group. The weights were measured after the respective aging periods ($m2$). Thorough desiccation and drying under heat and vacuum were done as described previously. The final weights after solvent drying werenoted ($m3$). The sorption and solubility in water (a measure of hydrolytic stability) and organic solvents (a measure ofdiffusivity resistance) at the respective specific times were calculated using the Equations 1-5.

Statistical Analysis
One-way ANOVA and Student's t-test with Bonferroni correction wherever more than five comparisons were done were used as the statistical tools to assess the significance at an alpha error of 0.05 and confidence level of 95%.

Results
MATRICES
Thermal Analysis
Thermo Gravimetric Analysis (TGA): A single thermal weight loss episode was noticed at 120^0 C leading to a reduction in weight by 16-18%. Thermal decomposition of the material started at 260^0 C and was complete by 510^0 C. No significant difference was noticed between the groups. (Fig 4)
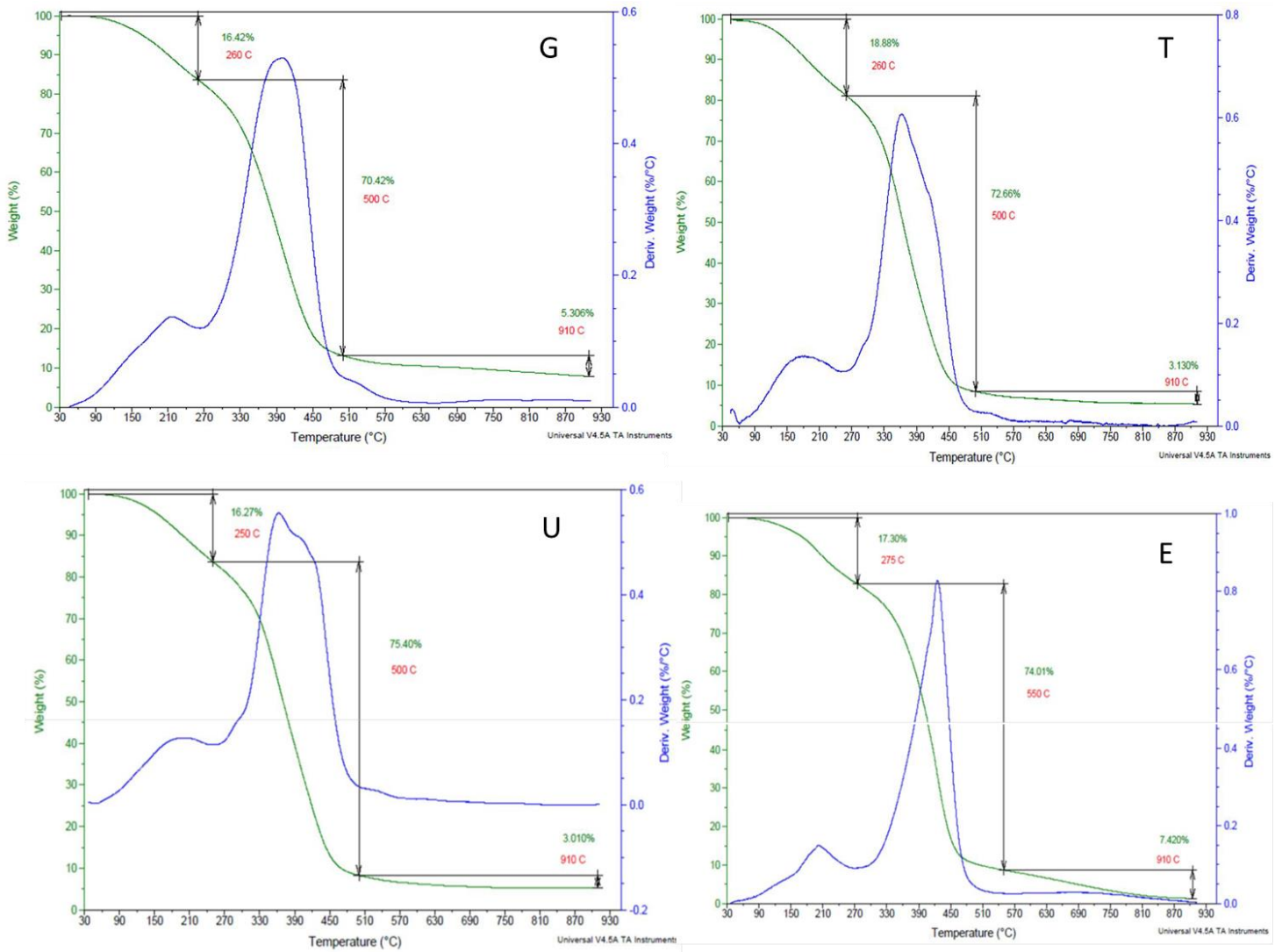
Fig. 4: TGA of experimental polymerized matrices

The glass transition temperature Tg was noticed at approximately 150⁰ C in the heating curve and confirmed by a slump in cooling curve peak. No other thermal incidents were noticed. No enthalpy changes occurred throughout the DSC. No melting points were observed confirming the amorphous nature of the matrix resins. However there was a second Tg at approximately -20⁰ C. This signal was comparatively weaker than the one at higher temperature. There was no significant difference in Tg between the different experimental groups. (Fig 5)
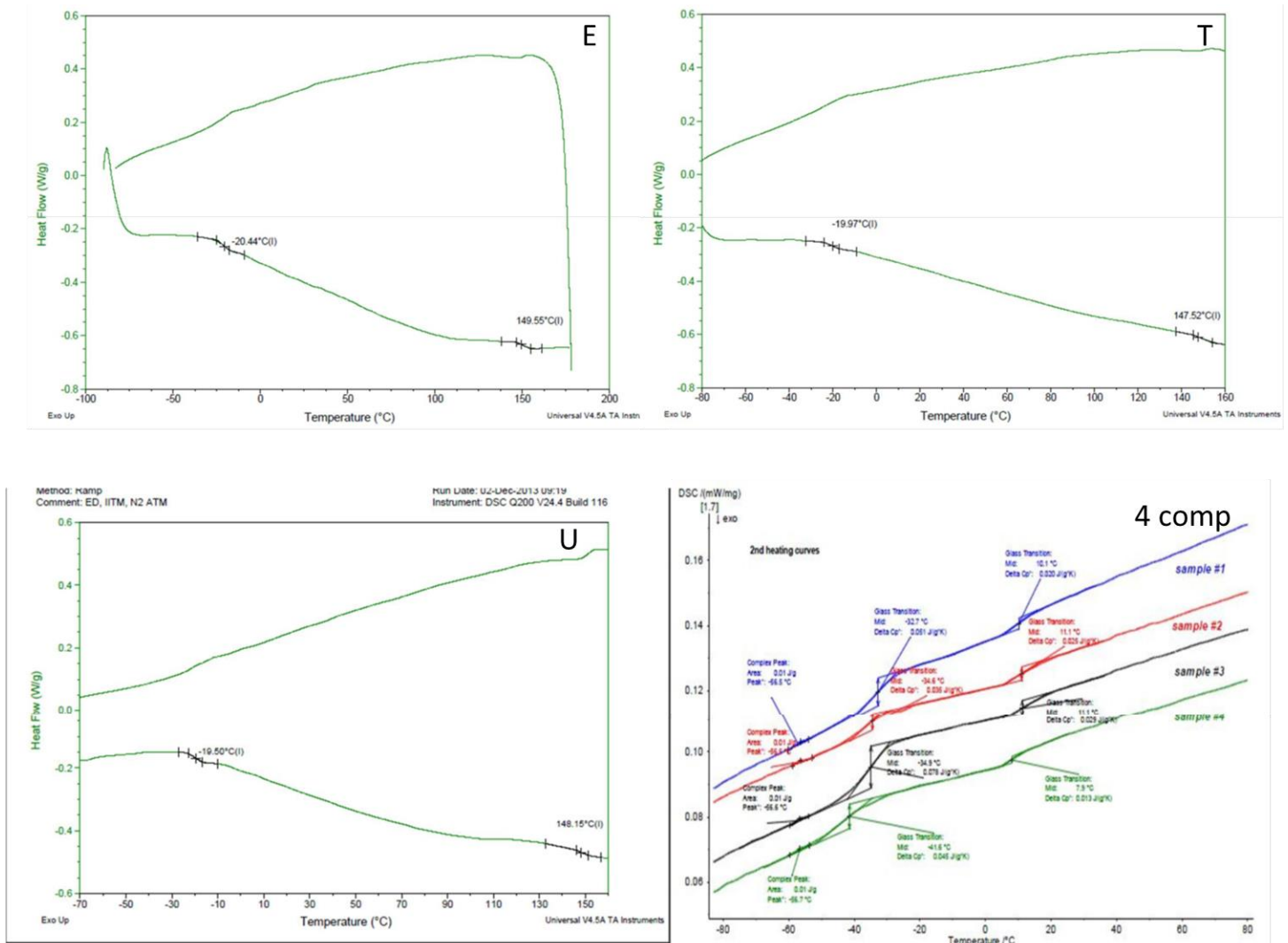
Fig. 5: DSC of experimental polymerized matrices & unpolymerized composites

Legend: Top left- DSC of polymerized matrix containing BisEMA; Top right- DSC of polymerized matrix containing TEGDMA; Above left- DSC of polymerized matrix containing UDMA; Above right- DSC of unpolymerized composites-sample #1 (blue) –composite U; sample #2 (red) – composite E; sample #3 (black) – composite G; sample #4 (green) – composite T

Hydrolytic Stability and Diffusivity Resistance
Groups BisGMA (G) and UDMA (U) containing matrices were showing significantly lower solubility than all the other groups (p=0.032-0.0001). Group TEGMA (T) containing matrix showed significantly less sorption than BisEMA (E) containing matrix (p=0.017), G (p=0.023) and U (p=0.007). There was no significant difference between the other groups. (Table 1)
Barring matrix U no other experimental group showed apparent sorption, which was however, very negligible. Matrices T and E showed more apparent solubility than matrix G, but it was not

statistically significant. Matrix U did not show any apparent solubility. Group U showed the least total sorption compared to the other groups. Since the apparent sorption was either nil or negligible, the apparent solubility and total sorption matched for allthe experimental groups. (Table 1)

Cross-link Density: Group E had the highest cross-link density. There was no statistically significant difference between groups U and G. There was a significant difference between the other groups and groups U or G. (Table 1)

Composites
THERMAL ANALYSIS
The polymerization reaction was observed as exothermic peaks in the photo-DSC. The largest enthalpy was associated with the first irradiation pulse for all the four experimental composites, with a gradual decline in the enthalpy with subsequent irradiations. (Fig 6)

Fig. 6: photo-DSC of experimental composites

The total enthalpy was calculated as a sum of all corrected (subtracted) enthalpic effects where the enthalpy of the subsequent irradiation was subtracted from the previous one. It was significantly different between the four groups. (Table 1) The Degree of conversion ranged from 95-99% and there was no significant difference between the groups. (Fig 7)

Fig. 7: Degree of Conversion of experimental composites by photo-DSC

Table 1 Cross-link Density, Diffusivity resistance of polymer matrices, Enthalpy of polymerization & Hydrolytic stability of composites

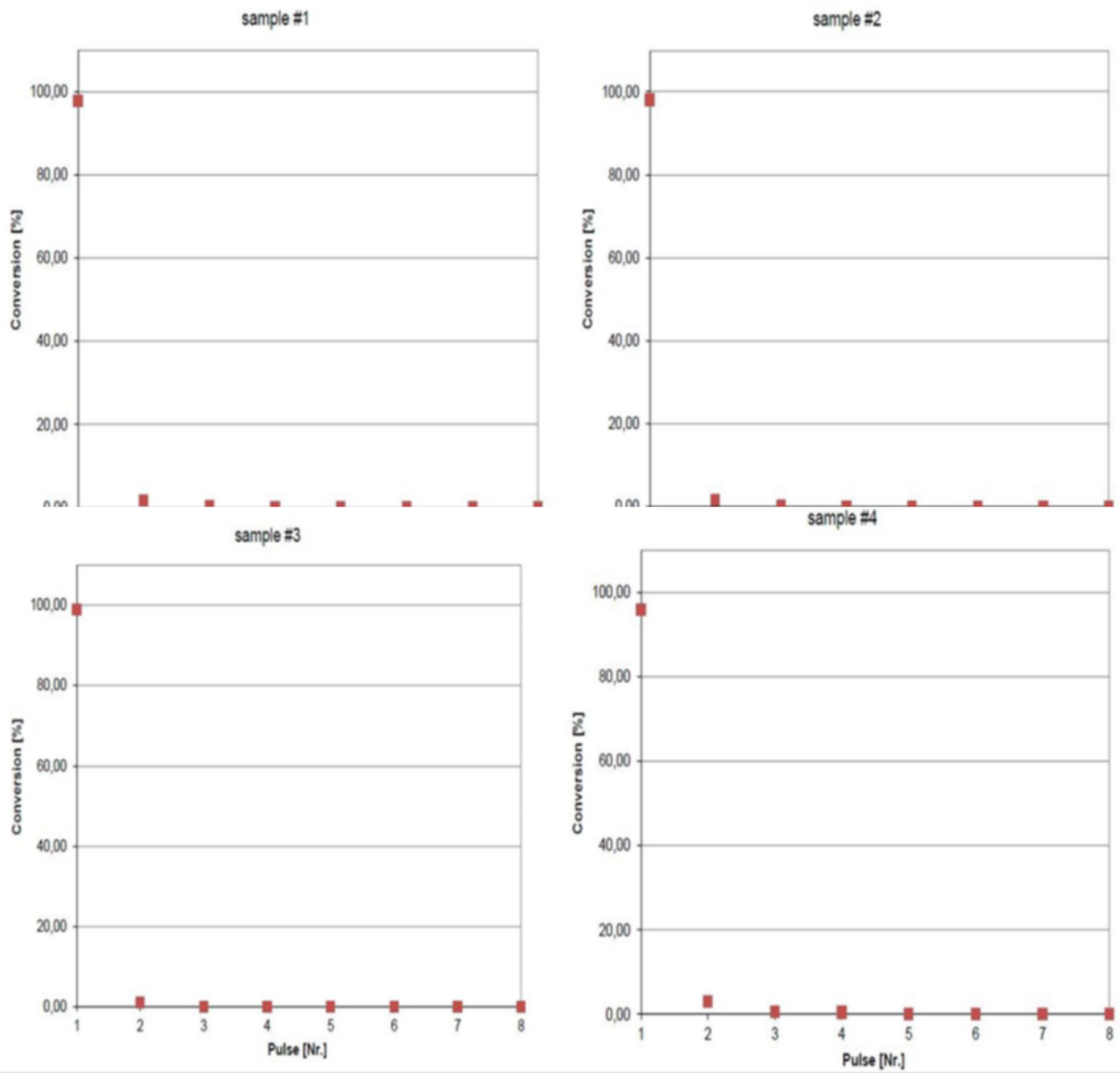| Group	Cross-link Density (polymer) mol/cm³	Enthalpy (composite) (J/g)	Diffusivity Resistance of polymer matrices — Sorption & Solubility in Organic Solvent (THF)					Hydrolytic stability of composites — Water Sorption & Solubility		
			Absolute sorption $S(120h)$ Mean µg/mm³ (S.D)	Absolute solubility $SL(120h)$ Mean µg/mm³ (S.D)	Apparent sorption Mean $M_g\%(120h)$ (S.D)	Apparent solubility Mean $SL\%(120h)$ (S.D)	Total sorption Mean $S\%(120h)$ (S.D)	Absolute sorption $S(120h)$ Mean µg/mm³ (S.D)	Apparent sorption Mean $M_g\%(120h)$ (S.D)	Total sorption Mean $S\%(120h)$ (S.D)
U	1.05×10^6 a	15.71^{d}	289.5^{g} (32.6)	290^{g} (17.6)	0.35^{CDI} (0.17)	0	0.35^{CDI} (0.17)	11.7^{lv} (2.03)	0.6^{D} (0.01)	0.6^{D} (0.01)
T	2×10^6 b	24.09^{e}	174.8^{h} (20)	435.2^{i} (22.4)	0	31.04^{A} (5.89)	31.04^{A} (5.89)	27.68^{m} (2.17)	1.13^{E} (0.12)	1.13^{E} (0.12)
E	7.1×10^7 c	17.94^{df}	236.9^{i} (18.4)	377.8^{k} (21)	0	29.63^{AB} (5.74)	29.63^{AB} (5.74)	31.5^{mu} (2.3)	1.74^{G} (0.18)	1.74^{G} (0.18)
G	1.3×10^6 a	19.9^{f}	235.5^{i} (21.5)	275.6^{g} (17.4)	0	20.09^{B} (4.6)	20.09^{B} (4.6)	7.95^{lx} (1.72)	0.35^{CI} (0.05)	0.35^{CI} (0.05)

Table 2 Diffusivity resistance of composites in Acetone

Group	Absolute solubility $SL(t)$ Mean µg/mm³ (S.D)			Apparent solubility Mean $SL\%(t)$ (S.D)			Total sorption Mean $S\%(t)$ (S.D)		
	$SL(1h)$	$SL(24h)$	$SL(1mo)$	$SL\%$ (1h)	$SL\%$ (24h)	$SL\%$ (1mo)	$S\%$ (1h)	$S\%$ (24h)	$S\%$ (1mo)
U	0.39^{n} (0.06)	25.07^{mt} (3.8)	62.1^{p} (7.6)	0.02 (0.01)	1.5^{EGK} (0.71)	3.73^{GH} (1.15)	0.02^{F} (0.01)	1.5^{EGK} (0.71)	3.73^{GH} (1.15)
T	1.99^{o} (0.4)	36.62^{mu} (9.8)	90.36^{q} (3.7)	0.08^{F} (0.05)	1.52^{EGK} (0.54)	3.76^{GH} (1.23)	0.08^{F} (0.05)	1.52^{EGK} (0.54)	3.76^{GH} (1.23)
E	7.16^{lx} (2.5)	62.5^{pr} (8)	91.16^{q} (7.9)	0.36^{CDI} (0.15)	3.14^{GH} (1.06)	4.59^{H} (1.56)	0.36^{CDI} (0.15)	3.14^{GH} (1.06)	4.59^{H} (1.56)
G	0.39^{n} (0.09)	50.55^{p} (7.7)	76.03^{r} (9.1)	0.02^{F} (0.01)	2.63^{G} (0.98)	3.97^{GH} (1.47)	0.02^{F} (0.01)	2.63^{G} (0.98)	3.97^{GH} (1.47)

Legend: (all tables)
U, T, E, G – Binary macromer containing matrix/composite with one of the four dimethacrylates UDMA(U), TEGMA(T), BISEMA(E), BISGMA(G);
Same superscript alphabets indicate no statistically significant difference invalues

In tetrahydrofuran, material G showed no solubility at all the time intervals, while material T showed none at 1h, whereas E showed only 1 month. Material U showed the highest solubility for all the time intervals. (Table3)

Table 3 Diffusivity resistance of composites in THF

Group	Absolute sorption S(t) Mean µg/mm³ (S.D)			Absolute solubility SL(t) Mean µg/mm³ (S.D)			Apparent sorption Mean $M_g\%(t)$ (S.D)			Apparent solubility Mean $SL\%(t)$ (S.D)			Total sorption Mean $S\%(t)$ (S.D)		
	S(1h)	S(24h)	S(1mo)	SL(1h)	SL(24h)	SL(1mo)	$M_g\%$ (1h)	$M_g\%$ (24h)	$M_g\%$ (1mo)	SL% (1h)	SL% (24h)	SL% (1mo)	S% (1h)	S% (24h)	S% (1mo)
U	0	0	0	20.3[t] (4)	36.62[u] (5.8)	56.92[p] (3)	0	0	0	1.41[K] (0.08)	2.54[G] (0.59)	6.49[J] (1.05)	1.41[K] (0.08)	2.54[G] (0.59)	6.49[JM] (1.05)
T	15.92[s] (1)	0	0	0	16.32[lst] (7)	17.51[stv] (6)	0.74[D] (0.24)	0	0	0	0.76[DE] (0.26)	0.82[EM] (0.23)	0.74[DM] (0.24)	0.76[DE] (0.26)	0.82[EM] (0.23)
E	25.87[t] (1.5)	28.66[mt] (3.1)	0	0	0	12.3[lsv] (4.1)	1.42[EGK] (0.22)	1.58[EGK] (0.3)	0	0	0	0.68[CDM] (0.31)	1.42[EGK] (0.22)	1.58[EGK] (0.3)	0.68[CDM] (0.31)
G	15.92[s] (1)	0	0	0	0	0	0.9[EM] (0.17)	0.19[I] (0.11)	0.99[EM] (0.35)	0	0	0	0.9[EM] (0.17)	0.19[I] (0.11)	0.99[EM] (0.35)

Table 4In chloroform, solubility was detected for all the materials only at 1 month, with U being the highest and G andE being the lowest. Table 4)

Table 4 Diffusivity resistance of composites in CHCl₃

Group	Absolute sorption S(t) Mean µg/mm³ (S.D)			Absolute solubility SL(t) Mean µg/mm³ (S.D)			Apparent sorption Mean $M_g\%(t)$ (S.D)			Apparent solubility Mean $SL\%(t)$ (S.D)			Total sorption Mean $S\%(t)$ (S.D)		
	S(1h)	S(24h)	S(1mo)	SL(1h)	SL(24h)	SL(1mo)	$M_g\%$ (1h)	$M_g\%$ (24h)	$M_g\%$ (1mo)	SL% (1h)	SL% (24h)	SL% (1mo)	S% (1h)	S% (24h)	S% (1mo)
U	63.69[pr] (5)	57.32[p] (6)	0	0	0	138.53[w] (21)	4.03[H] (0.21)	3.62[GH] (0.81)	0	0	0	8.77[M] (1.42)	4.03[H] (0.21)	3.62[GH] (0.81)	8.77[M] (1.42)
T	93.55[q] (4.6)	126.99[w] (19)	0	0	0	65.68[pr] (9.5)	5.02[J] (1.06)	6.82[JM] (1.01)	0	0	0	3.53[GH] (0.77)	5.02[J] (1.06)	6.82[JM] (1.01)	3.53[GH] (0.77)
E	133.35[w] (5.7)	96.73[q] (7)	0	0	0	35.82[m] (7.4)	7.02[JM] (1.17)	5.09[J] (0.95)	0	0	0	1.88[EGK] (0.62)	7.02[JM] (1.17)	5.09[J] (0.95)	1.88[EGK] (0.62)
G	75.23[r] (8)	74.84[r] (8)	0	0	0	35.03[mu] (8)	4.51[H] (1.09)	4.49[H] (0.53)	0	0	0	2.1[G] (0.91)	4.51[H] (1.09)	4.49[H] (0.53)	2.1[G] (0.91)

In carbon tetrachloride, composite G did not show any solubility at any of the time intervals and materials Uand E showed only at 1h with U being significantly lower. (Table 5)

Table 5 Diffusivity resistance of composites in CCl4

Group	Absolute sorption $S(t)$ Mean μg/mm^3 (S.D)			Absolute solubility $SL(t)$ Mean μg/mm^3 (S.D)			Apparent sorption Mean $M_g\%(t)$ (S.D)			Apparent solubility Mean $SL\%(t)$ (S.D)			Total sorption Mean $S\%(t)$ (S.D)		
	$S(1h)$	$S(24h)$	$S(1mo)$	$SL(1h)$	$SL(24h)$	$SL(1mo)$	$M_g\%$ $(1h)$	$M_g\%$ $(24h)$	$M_g\%$ $(1mo)$	$SL\%$ $(1h)$	$SL\%$ $(24h)$	$SL\%$ $(1mo)$	$S\%$ $(1h)$	$S\%$ $(24h)$	$S\%$ $(1mo)$
U	0	13.13^{ls}(3.1)	23.48^{msu}(7)	3.58^{oxy}(1.2)	0	0	0	0.81^{DM} (0.13)	1.41^{EGK} (0.51)	0.21^{I} (0.02)	0	0	0.21^{I} (0.02)	0.81^{DM} (0.13)	1.41^{EGK} (0.51)
T	0	6.36^{lox}(4)	0	8.75^{lx}(2.7)	0	3.58^{y} (0.63)	0	2.99^{G} (0.72)	0	0.37^{CI} (0.05)	0	0.15^{L} (0.02)	0.37^{CI} (0.05)	2.99^{G} (0.72)	0.15^{L} (0.02)
E	0	9.15^{lx}(3.5)	23.88^{t}(3)	8.35^{lxy}(4)	0	0	0	0.47^{CD} (0.08)	1.24^{EG} (0.36)	0.43^{CD} (0.06)	0	0	0.43^{CD} (0.06)	0.47^{CD} (0.08)	1.24^{EGK} (0.36)
G	6.76^{xy}(2)	48.56^{pu}(8)	34.63^{mu}(5)	0	0	0	0.41^{DL} (0.25)	2.99^{G} (0.72)	2.13^{G} (0.49)	0	0	0	0.41^{CL} (0.25)	2.99^{G} (0.72)	2.13^{G} (0.49)

In tetrahydrofuran composite U did not show any sorption at any of the time intervals, while composite T sorbed only at 1h. Only composite G sorbed at 1 month and overall, composite E showed the highest sorption at1 and 24h. (Table 3)

In chloroform none of the materials sorbed at 1 month, while composite E showed the highest at 1h andcomposite T at 24h. (Table 4)

In carbon tetrachloride, barring composite G none of the materials sorbed at 1h, and it continued to show the highest sorption at all the time intervals, whereas T showed comparatively lower sorption and that too only at24h. (Table 5)

Apparent Sorption and Total Sorption of Composites:
In deionized water, composite E showed the highest apparent and total sorption while composite G the lowest. (Table 1) Since the solubility was nil, apparent and total sorption values were similar.

None of the experimental composites showed apparent sorption in acetone at any of the time intervals tested.(Table 2)

At 1h, only composite G showed apparent sorption in carbon tetrachloride, (Table 5) while U showed none in tetrahydrofuran. Composite E showed the highest apparent sorption in tetrahydrofuran and chloroform. (Table3)
At 24h, composite T showed more apparent sorption in chloroform, (Table 4) while composite G showed more apparent sorption in carbon tetrachloride (Table 5) and E in tetrahydrofuran. Composites U and T did not show any apparent sorption in tetrahydrofuran. (Table 3)

At 1 month, no apparent sorption was detected for all the materials in chloroform. (Table 4) In carbon tetrachloride, composite G showed more apparent sorption and T showed none. (Table 5) In tetrahydrofuranonly composite G showed apparent sorption. (Table 3)

The apparent solubility was very minimal for all the composites in all the solvents at 1h. While composite U showed the highest at 24h and 1 month in tetrahydrofuran and chloroform. (Tables 3 & 4)

The total sorption % profile of the composites was the lowest at 24h for acetone, (Table 2) and in tetrahydrofuran at 24h and 1 month. (Tables 3) Composite U showed the highest value in carbon tetrachloride at1 month, followed by E at 1h in the same solvent. While composite T showed the highest value at 24h in the same solvent. (Table 5)

Discussion

Thermal and hydrolytic stability of the restorative materials help in their longevity in oral cavity which exposes them to extreme thermal differentials (sizzling brownies, hot coffee, frozen dessert etc.) with very little time differential between the exposures and ionic, aqueous and alcoholic challenges like cocktails and mocktails etc. If the restorative materials do not exhibit stability, they would leach out harmful moieties that can endanger even systemic health.

In the present study, the thermal decomposition of the matrices started at a fairly high temperature indicative of the thermal stability of the experimental materials and there was no significant difference between the experimental groups based on different dimethacrylates as co-polymers. During polymerization reaction, stress relaxation is an important criterion to preserve bonding with dental tissues and prevent enamel/dentin cracks. The dual Tg observed in both polymerized resin matrices and unpolymerized composites could probably be due to the presence of tough and flexible polymer portions arising out of co-polymerization of two different macromers with dimethacrylates. Thus the amorphous characteristic of the experimental polymer network indicates that they have good stress relaxation in post-gel stage. This would not only allow better stress relaxation during polymerization reaction but also ensure that the modulus and strength are optimal. Though unpolymerized composites showed a significant difference in the higher Tg based on the type of dimethacrylates used, with T being the lowest and U being the highest, polymerized matrices did not show any such difference. This may probably be due to the cross reaction of the dimethacrylate with the free radical polymerizable macromer and consumption of significant number of double bonds. The Tg of methacrylate based polymerized matrices have been found to vary between 45-53^0 C depending upon the monomer ratios used and the curing irradiance[9]. The Tg of oligomeric and monomeric thiol-ene polymers were found to vary from 29 to 49^0 C.[10] The Tg of thiol-ene oligomer containing composites was found to be 64^0 C. [11]The organic matrix used in the present study however showed a higher Tg at 150^0 C. In a previous study, monomer tris(4-hydroxyphenyl) methane triglycidyl methacrylate (TTM) based composite and a control composite showed a Tg of 132^{0}C [12] closer to the values recorded in the present study.

While polymerizing conventional composites, the temperature rise on the pulpal side of cavity

preparations was approximately 6^{0}C, irrespective of the composite type or curing device [13] Such rise is related to the irradiance power of the curing unit [14] and the enthalpy of polymerization of the composite. Light curable composites and pulp capping agents have shown a 3.5^{0}C increase in pulpal temperature after light activation, when placed in close proximity to pulp and 2.1^{0}C, when separated by 1mm of dentin.[15] In the present study, the photo-DSC analysis showed an enthalpy of 15-28J/g for the four experimental composites during polymerization. There was a significant difference between the groups with U being the lowest and T being the highest. However, even this is approximately two times less than that observed in commercial cationic ring opening polymerizable (75 J/g) composites and a little less than that of free-radical polymerized (31 J/g) composites.[16,17] The post-cure[18]

Optical pyrometry studies on oxiranes have shown 100 ^{0}C rise in temperature during the exothermic polymerization. [19] However, there would not be dangerous rise of temperature in the dental pulp or periodontal ligament during the polymerization reactions of experimental composites studied, since their measured enthalpies are much lower.

Resin-based materials used in dentistry undergo water degradation, due to plasticization and hence assessing the hydrolytic stability is paramount in selecting a restorative material for potential application in dentistry. In the present study at 120h the water sorption of the experimental materials varied between 7.9-31.84μg/mm^3. The water sorption and solubility of methacrylate based, oxirane based and Silorane based materials were investigated by Palin and others and it was found that Silorane based material had the lowest sorption of 0.52-3.92μg/mm^3 in a 10min-48h period, while methacrylate had intermediate values of 0.54- 10.56μg/mm^3 whereas those of oxirane were the highest at 0.096-15.42μg/mm^3 during the same period.[20] The difference in sorption values of the present study could be due to the longer duration of immersion, implying that the experimental composites are fairly resistant to hydrolytic disintegration. In another study on water sorption of different composites cured under different modes and light sources, standard halogen curing resulted in similar values as that of the present study. However, in another study on water sorption of organosilicon based dental composites containing Bis Acryloxymethyl phenethyl tetramethyl disiloxane after 1 week immersion, the values were lower[21] than the present study .

Similarly, in a study on water sorption of a new dimethacrylate based on benzophenonetetra-carboxylic dianhydride (BTDMA), the values reached a plateau for BisGMA based materials faster (10days) than the monomer BTDMA. Further BTDMA sorbed more than BisGMA based material.[22] However, the sorption of composites made of 2-ethyl hydroxy methacrylate containing bis di isocyanate resin matrix (2EMATE-BDI) [23]have been shown to to be similar to those reported in the current study. In another study, a lower sorption value[12] was observed, for a tris(4-hydroxyphenyl) methane triglycidyl methacrylate (TTM) based composite. But, the sorption of different resin adhesive cements[24] from 1h to 168h of immersion in water containing lactic acid was found to be similar to those of the present study, though the water used in the present study was neutral pH.

In a study on apparent sorption (Mg%) of BisGMA based composites with differently surface-treated hydroxyapatite fillers after 2 weeks immersion in water, it was found that 40% TEGDMA addition resulted in sorption values approximately 1.5-7.5%, while 40% HEMA addition, resulted in almost double that value[25]. In the present study, the Mg% varied between 0.3-1.7% and the total sorption (S%) 0.96-1.69% for different resin-based adhesive cements between 0.2-1.7% which are comparatively less. One study showed that the Mg% at 168h varied between 0.89-1.5 and thetotal sorption (S%) 0.96-1.69% for different resin-based adhesive cements.[26] These conform to the values reported in the present study.

Solubility of methacrylate based, oxirane based and Silorane based materials were investigated by Palin and others and it was found that Silorane based material had 0-0.24μg/mm^3, methacrylate had 0.08-0.7μg/mm^3 for and oxirane18 had 0.09-2.2μg/mm^3 values. Solubility of composites[22] have been shown to range from 1-3 μg/mm3 when 2-ethyl hydroxy methacrylate containing bis di isocyanate resin matrix (2EMATE-BDI) was compared to UDMA or BisGMA containing resin composites, to 0.5-0.9 μg/mm3 when a tris (4-hydroxyphenyl) methane triglycidyl methacrylate (TTM) based composite and a BisGMA composite was compared.[12] The solubility of different resin adhesive cements [24] from 1h to 168h of immersion in water containing lactic acid was varied from 1.5-2.3 μg/mm^3. In the present study there was no solubility for any of the experimental materials at 120h immersion.

In a study on apparent solubility (SL%) of BisGMA based composites with differently surface-treated

hydroxyapatite fillers after 2 weeks immersion in water, it was found that 40% TEGDMA/HEMA addition resulted in 0.5-5.5% and 1-12% respectively.[25] One study showed that the SL% varied between 0.07-1.3 at 168h for different resin-based adhesive cements immersed in lactic acid containing water.[26] Since the experimental materials tested in the present study did not show any apparent solubility, the hydrolytic stability of the experimental materials appears to be superior. Diffusivity resistance of materials made of polymers indicates the resistance of the network to allow plasticization and subsequent elution in organic solvents or media. In an attempt to characterize the experimental materials' diffusivity resistance and cross-link density and network stability strong organic solvents were chosen in the present study. The sorption of the experimental organic matrices ranged between 150-300µg/mm^3 in tetra hydro furan after 120h immersion. Strong organic solvents like this were chosen in the present study to test the network stability. TEGDMA containing matrix (T) showed significantly less sorption.

Also the sorption and solubility of the experimental composites in the 4 organic solvents was lower. In Tetra Hydro Furan and chloroform, the solubility of group U was greater than others. This group had UDMA in the composition and this dimethacrylate has probably less resistance to dissolution in these solvents. However, it should be noted that the greatest dissolution occurred only at the longest immersion period (1 month). Solubility in carbon tetra chloride was the lowest among the solvents. Groups T and E showed greater solubility indicating the affinity for TEGDMA and BisEMA for this solvent over the other dimethacrylates. Acetone was the only solvent capable of dissolving all the four dimethacrylates containing experimental composites at all the time intervals tested. Sorption in THF was considerably lower whereas chloroform the highest. Again, it is noteworthy that all the higher values were observed only for the longest immersion period (1 month) and this finding underlines the good stability of the experimental materials in a wide variety of polar and non-polar solvents.

The cross-link density, measured as a function of the stability of the polymerized matrices in organic solvent, was high for all experimental materials, with group E being the highest (10 times more at 7.1X10^7 mol/cm3). The reported value for similar polymer based materials in the literature is 2.5X10^6 mol/cm^3. In the present study, the direct cross-link density assessment of polymer matrices was carried out, whereas many studies have

carried out indirect assessment by hardness reduction after ethanol storage of composites [27,28]. High cross-link density of the experimental materials would have ensured higher diffusivity resistance such that their stability in a range of polar and non-polar solvents is high which has been confirmed by the results of sorption and solubility in various solvents.

Conclusions
The experimental materials composed of two amorphous macromers co-polymerized with different dimethacrylates, showed promising thermal behavior, hydrolytic stability, cross-link density and increased ability to resist disintegration in polar and non-polar solvents, implying a high diffusivity resistance. Additionally, their enthalpies of polymerization were significantly lower than those of contemporary materials. Hence these can be developed as potential restorative dental composites after testing for other relevant properties.

Conflict of Interest
The authors declare that they do not have any competing interests in the above research work and its manuscript preparation

Clinical Significance
- Macromers offer hydrolytic stability for dental composites
- Amorphous macromers have not been tried in dental composites till date

- Binary amorphous macromers co-polymerizable with dimethacrylates have been tested
- Experimental matrices and composites based on a patented material with the above principle shows promising thermal

and hydrolytic stability
- Such materials can be potentially used in dental composites for durable restorations

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