ORIGINAL RESEARCH

Chemical Characterization and Physical Properties of Dental Restorative Composite Resin with a Novel Multifunctional Cross-linking Comonomer

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ABSTRACT

Aim and objective: To chemically characterize restorative composite resin polymerized with 20 wt.% and 40 wt.% dipentaerythritol penta-/hexaacrylate (DPEPHA) comonomer. Furthermore, this study aimed to evaluate the conversion degree (DC) and glass transition temperature ($T_g$) of the newly formed copolymer.

Materials and methods: The trial groups were photo-polymerized with DPEPHA comonomer, whereas the control group was photo-polymerized only with the propriety resin monomers. Infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies were used for establishing copolymerization. The characteristics and composition (mass %) of the surface were explained by field-emission scanning electron microscopy (FESEM) and energy-dispersive X-ray (EDX) spectroscopy, respectively. The DC and $T_g$ of the resultant copolymers were evaluated through FTIR and differential scanning calorimetry, respectively. Appropriate statistical tests with corresponding post hoc tests were employed to compare the medians and means of DC and $T_g$, respectively.

Results: The formation of a new copolymer P(GEU-Co-DPEPHA) was evident. The DC and $T_g$ of the P(GEU-Co-DPEPHA) copolymer were greater than the control. DPEPHA in the copolymer at 40 wt.% concentration showed the highest DC and $T_g$.

Conclusion: DPEPHA comonomer addition leads to the formation of a new P(GEU-Co-DPEPHA) copolymer with improved DC and $T_g$.

Clinical significance: The novel P(GEU-Co-DPEPHA) copolymer may improve the physico-mechanical and biological properties of the restorative composite resin. This would improve the quality of restoration and its in vivo serviceability, thereby imparting a good living quality to the entailed population.

Keywords: Copolymer, Cross-linker, Degree of conversion, Dipentaerythritol penta-/hexaacrylate, Glass transition temperature.

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INTRODUCTION

2,2-bis-[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane or bisphenol-A-glycerolate dimethacrylate (bis-GMA; G), bisphenol-A-ethoxylate dimethacrylate (bis-EMA), 1,6-bis-(methacryloyloxy-2-ethoxycarbonylamo)-2,4,4-trimethylhexane, known as urethane dimethacrylate monomer (UDMA; U), and triethylene glycol dimethacrylate (TEGDMA; E) are the frequently employed dental dimethacrylate monomers. Copolymerization of these dimethacrylate monomers in mixtures of various ratios has been achieved. Myriad commercial dental composite resins are based on these exemplary mixtures of dimethacrylates.

Low degree of conversion (DC) and reduced possibility of filler addition are primarily due to the extreme viscosity of bis-GMA. Oligoethylene glycol dimethacrylates (TEGDMA; a low-molecular-weight dimethacrylate) are being used to decrease this viscosity and increase the DC and filler load. A rise in polymerization shrinkage, however, is caused by the addition of TEGDMA. Bis-EMA and UDMA monomers were developed in response to flaws in bis-GMA. The molecular weights of these monomers are akin to bis-GMA, but with low viscosity. Bis-EMA is less viscous than UDMA, with no hydroxyl groups. Without the use of reactive diluents, a combination of bis-GMA and bis-EMA can be used. The viscosity of the UDMA monomer is amplified by the intermolecular hydrogen bonds between urethane species. It is the only dimethacrylate that can

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be employed discretely as commercial composite matrix due to the acceptable mechanical properties of its homopolymers. It can also be synergistically used with bis-GMA as a thinner.

Unresolved problems in radical polymerization of dimethacrylates include incomplete conversion of double bonds and microgel agglomeration. DC is never complete in such spatially heterogeneous polymer networks containing agglomeration with cross-link density variations. Traditionally, composite dental materials achieve a DC of about 50 to 75%. In homopolymer networks of spacious dimethacrylates, such as bis-GMA, the limited conversion can be as low as 50%. Because of the presence of a sol fraction, polymer networks with a DC less than 50% are unsuitable for practical applications. Some authors recommend a DC of at least 55% for clinical success in dentistry. Recently, characterization of the structural heterogeneity of dimethacrylate polymeric networks has been determined quantitatively by the thermal analysis techniques. In the differential scanning calorimetry (DSC) studies to assess glass transition temperature ($T_g$), changes in heat capacity during glass transition and curing enthalpy are evaluated. $T_g$ is the temperature at which the characteristics of the monomer shift from glass to rubber; the available polymer movements are limited below the glass transition temperature. However, above the glass transition, a motion that begins with one atom will pass through the chain and cause detrimental effects on the polymer chains. Therefore, DC and $T_g$ are vital parameters governing the in vivo serviceability of restorative composite resins.

Monomeric modifications were not uncommon with acrylic resins that were executed to enhance the physico-mechanical and biological properties of dental restorative composites. However, some pitfalls to be solved remain in the restorative matrix monomers, such as low monomer conversion rate, high polymerization shrinkage, aging, and degradation during service. Therefore, new types of monomers have been developed to meet these deficiencies.

Dipentaerythritol penta-/hexaacrylate (DPEPHA) is a novel multifunctional hydrophobic monomer possessing cross-linking ability, abrasion resistance, surface hardness, and good adhesive property. Phosphorylated form of DPEPHA (phosphate ester monomer) has been used as bonding agents to lute zirconia crowns to the teeth. However, there are no researches available regarding the use of non-phosphorylated DPEPHA in the dental restorative composite resins. Hence, the present research seeks to develop and evaluate a novel dental composite containing DPEPHA as comonomer.

However, the interaction and copolymerization of the added comonomer with the propriety matrix resin monomers (bis-GMA, TEGDMA, and DUDMA [GEU]) play a vital role as copolymerization determines the properties of the dental restorative composite resins. To enhance the properties of the dental restorative composite with a comonomer, it warrants a prominent interaction between the propriety matrix monomers and the added comonomer. Therefore, the present research aims to characterize and evaluate the physical properties of the photo-activated dental resin composite with DPEPHA.

**Materials and Methods**

Fourier transform infra-red (FTIR), nuclear magnetic resonance (NMR) spectroscopies, and field-emission scanning electron microscopy (FESEM) of the specimens were performed at Central Electro-Chemical Research Institute, Tamil Nadu. Differential scanning calorimetry (DSC) and energy-dispersive X-ray spectroscopy (EDX) were executed at Centralized Instrumentation and Service Laboratory, Annamalai University, Tamil Nadu. Table 1 describes the materials used in the research.

**Matrix Formulation and Photo-polymerization of Control and Trial Groups**

The composition of composite matrices of control (G0) and trial groups (G20 and G40) was given in Table 2. The total matrix: filler ratio was 30:70 wt.%. For control matrix (G0), bis-GMA was taken and stirred at 40°C for 10 minutes in an ultrasonic bath. Subsequently, TEGDMA and DUDMA were added. For G20 and G40, DPEPHA was additionally incorporated at 20 wt.% and 40 wt.%, respectively. To this mixture, CQ and DMAEMA were added at a ratio 1:2 and stirred for 3 hours. Eventually, 70 wt.% pre-coupled fillers were incorporated into the resin matrix and stirred for 24 hours. The entire formulation was dried at 37°C in vacuum for 30 minutes and incubated at room temperature until further use.

The matrix material was placed in a Teflon mold with typical dimensions (15 mm diameter, 1 mm thick, $n = 10$ per group for DC by FTIR spectroscopy). To remove the surfeit matrix material, the DC less than 50% are unsuitable for practical applications.

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**Table 1: Monomers and fillers used in the research**

| Material                          | Manufacturer                                           | Batch/Lot number |
|-----------------------------------|--------------------------------------------------------|-----------------|
| Bis-phenol-A glycerolate dimethacrylate | Sigma Aldrich Co., St Louis, MO, USA.                  | MKCF9832        |
| Triethylene glycol dimethacrylate  |                                                        | STHB8825        |
| 2-Diurethane dimethacrylate        |                                                        | MKCG8230        |
| Camphorquinone                     |                                                        | 09003AQV        |
| Dimethyl aminomethyl methacrylate  |                                                        | BCC3073         |
| Dipentaerythritol penta-/hexaacrylate |                                                        | MKCJ0750        |
| Barium oxide                       | Sisco research laboratories Pvt. Ltd., Maharashtra, India | 0000097407      |
| Barium fluoride                    |                                                        | 9409286         |
| Zirconia nanoparticles             | Nano Research Lab, Jamshedpur, Jharkhand, India         | 125-02          |

**Table 2: Composition of control and trial matrices**

| Matrix | Composition                                                                 |
|--------|-----------------------------------------------------------------------------|
| G0     | Monomeric ingredients: bis-GMA (50 wt.%), TEGDMA (20 wt.%), DUDMA (30 wt.%); GEU. Filler ingredients: BaO (30 wt.%), BaF₂ (30 wt.%), ZrO₂ (40 wt.%). The total CQ:DMAEMA (1:2) is 1 wt.% |
| G20    | Monomeric ingredients: bis-GMA (40 wt.%), TEGDMA (20 wt.%), DUDMA (20 wt.%), DPEPHA (20 wt.%). Filler ingredients: BaO (30 wt.%), BaF₂ (30 wt.%), ZrO₂ (40 wt.%). The total CQ:DMAEMA (1:2) is 1 wt.% |
| G40    | Monomeric ingredients: bis-GMA (30 wt.%), TEGDMA (20 wt.%), DUDMA (10 wt.%), DPEPHA (40 wt.%). Filler ingredients: BaO (30 wt.%), BaF₂ (30 wt.%), ZrO₂ (40 wt.%). The total CQ:DMAEMA (1:2) is 1 wt.% |
Composite with Dipentaerythritol Penta-/Hexaacrylate

a clear cellophane sheet was positioned onto the mold’s surface and pressed against a glass tile. The resin matrices were photo-polymerized from both sides for 40 seconds with a light-curing unit (Guilin Woodpecker Medical Instrument Co., Ltd.; Guangxi, China; absorbs light in the 420–480 nm, 650–800 mW cm$^{-2}$).

**FTIR Spectroscopy and Degree of Conversion**

The DC of the photo-polymerized specimens of all the groups was determined by FTIR spectroscopy in attenuated total reflection (FTIR-ATR) mode (Tensor 27 model; Bruker Optik, GmbH, Germany) with 4000 to 600 cm$^{-1}$ scanning range at 4 cm$^{-1}$ s$^{-1}$ speed and 64 scans in the final spectrum. First, the FTIR spectra of unpolymerized resin matrices of all the groups were obtained. The FTIR spectra of the photo-polymerized specimens were also measured. Since the organic phase of dental composite monomers is mainly dimethacrylates, the unreacted methacrylate groups were quantified using an absorption (Abs) band of 1638 cm$^{-1}$ (aliphatic C=C double bonds) and compared to the 1608 cm$^{-1}$ (C=C double bonds of bis-GMA’s aromatic ring) absorption band, which did not involve in the polymerization. DC was measured by comparing the peak height ratios of aliphatic C=C peak to aromatic C=C peak of polymerized specimens to the unpolymerized specimens. DC% was calculated using the following equation:

$$\text{DC\%} = \left(\frac{\text{Abs 1638}}{\text{Abs 1608}}\right)_{\text{Polymerized}} - \left(\frac{\text{Abs 1638}}{\text{Abs 1608}}\right)_{\text{Unpolymerized}} \times 100.$$

**NMR Spectroscopy**

A digital NMR spectrometer (Ascend™ 500; Bruker, GmbH, Germany) was used for recording $^1$H- and $^{13}$C-NMR spectra. For $^1$H- ($n = 1$ per group) and $^{13}$C-NMR ($n = 1$ per group), polymerized resin specimens were ground to fine powder. Later, 20 mg ($^1$H-NMR) and 30 mg ($^{13}$C-NMR) powdered resin specimens were dissolved in 1 mL of deuterated chloroform (CDCl$_3$) in a thin glass tube. Tetramethylsilane served as an internal standard.

**FESEM-EDX Spectroscopy**

For FESEM-EDX, one prototypical cuboidal specimen ($n = 1$ per group; $5 \times 5 \times 3$ mm$^3$) was photo-polymerized. The surface topography of the groups was analyzed using a FESEM (Carl Zeiss, Supra 55VP, Germany). The unfinished specimens were mounted on specimen stage, and the beam-specimen distance was adjusted to 10 mm. The chemical constituents of the specimens in mass percent were detected by EDX spectroscopy (JEOL-JSM-IT 200; Tokyo, Japan). The X-ray photon fusilladed the atomic electrons and was detected using EDX spectrometer. An in-built microanalysis software was used to process the graphical representation of the constituents (live analysis).

**Glass Transition Temperature**

For $T_g$, the specimens were analyzed in the differential scanning calorimetry (DSC) instrument (Netzsch, STA 449 F3 Jupiter®, Selb, Germany) under nitrogen. Each group had 10 photo-polymerized specimens ($n = 10$ per group), which were finely ground to powder. Powdered specimens (20 mg) were heated on an aluminum holder to temperatures ranging from 50°C to 200°C at a heating rate of 20°C min$^{-1}$. Both measurements were performed using data from the second cycle to erase the specimen’s thermal background.

Using the built-in program (Proteus®), the $T_g$ was measured by the technique described elsewhere.$^{2,1}$

**Statistical Analysis**

The data analysis was accomplished using the Statistical Package for the Social Sciences software (SPSS Inc., Chicago, IL, USA; version 21.0). According to Kolmogorov–Smirnov test, the data distribution concerning DC was not normally distributed and thus was presented as median and interquartile range. Kruskal–Wallis test was employed to analyze differences between the control and trial specimens, which was followed by post hoc Dunn’s test ($\alpha = 0.05$). Concerning $T_g$, the data were normally distributed and the continuous data were presented as mean and standard deviation (SD). The level of significance between the three groups for $T_g$ was tested with one-way analysis of variance (ANOVA). Post hoc Bonferroni test ($\alpha = 0.05$) was executed to compare the groups. $P < 0.05$ was considered for statistical significance.

**RESULTS**

**FTIR Spectroscopy**

Figure 1 highlights the spectral variations among the groups. The appearance of a peak at 1635.66 cm$^{-1}$ in G0 [P(GEU)] is attributed to aliphatic C=C stretch (zone II). Peak at 773.46 cm$^{-1}$ in G0 is attributed to cis-C=C bending of di-substituted alkene moiety (zone V). These peaks in G0 are not apparent in the case of trial groups G20 and G40. Absence of this peak in the G20 and G40 groups implies less or negligible presence of residual monomer content. In the trial groups G20 and G40, peaks at 810.01 cm$^{-1}$ are attributed to C–H bending corresponding to multi-substituted acrylate moiety, which are absent in the G0 group (zone V). Peak intensities decreased in the trial groups that were attributed to C–N amine stretching and N–H out-of-plane deformation of secondary aliphatic amine at zone IV and zone V. This indicates the reduction of DUDMA concentration in the trial groups. Peaks corresponding to carbonyl moiety (C=O stretch and C–H bend of O=C–H) at zone II and zone III are intensified for the trial groups when compared to G0. The intensified peak at zone I contributed to O–H stretching in the trial groups indicates the presence of alcohol moiety of the DPEPHA comonomer, which is of less significance.

![Fig. 1: FTIR spectral differences between the groups](image-url)
**NMR Spectroscopy**

The peak signals of $^1$H-NMR at δ 3.74 to 3.76 and δ 3.93 to 3.95 (\(-\text{C}-\text{CH}_2\text{-O-CH}_2\text{-C}\)) in the trial groups indicate the presence of DPEPHA. The peak signals of (–\(\text{CH}_2\text{-CH(O)O-}\)) at δ 6.13 to 6.14 (G20); δ 6.29 to 6.33 (G40) and (–\(\text{CH}_2\text{-CH-C(O)O-}\)) at δ 6.37 to 6.41 (G20); δ 6.72 to 6.74 (G40) also confirm the incorporation of DPEPHA in the resin matrix. The peak signals of $^{13}$C-NMR at δ 26.05 (G20); δ 29.70 to 29.30 (G40) for tertiary carbon (–\(\text{CH}_3\)), peak signal of (–\(\text{C}-\text{CH}_2\text{-O-CH}_2\text{-C}\)) at δ 31.11 (G20); δ 31.02 (G40), peak signals of (–\(\text{C}-\text{CH}_2\text{-O-CH}-\)) and (–\(\text{CH}_2\)) attached to acrylate moiety at δ 44.11 (G20); δ 43.82 (G40) indicate the presence of DPEPHA in the trial groups. Hence, the appearances of the abovementioned peak intensities in the trial groups attest to the copolymerization of DPEPHA with the propiety resin matrix (GEU) and the formation of a new copolymer P(GEU-Co-DPEPHA). These peak signals are absent in the G0. The peak signals at δ 5.69 and δ 6.24 in $^1$H-NMR; peak signal at δ 125.70 to 126.21 in $^{13}$C-NMR of G0 confirm residual monomer’s presence, which are absent in the trial groups. Figure 2 depicts the detailed schema of the newly formed copolymer P(GEU-Co-DPEPHA).

![Figure 2: Schema of newly formed copolymer P(GEU-Co-DPEPHA).](image)

**FESEM-EDX Spectroscopy**

FESEM analysis showed morphological differences between the control and trial groups. More homogenous material structure was observed in G40, whereas G0 presented a rough and irregular surface. G20 has an intermittent surface character between G0 and G40 (Fig. 3). Hence, the addition of DPEPHA enhanced the surface characteristics of the new copolymer P(GEU-Co-DPEPHA). The elemental composition in mass% of C, O, Zr, Ba, and F of control and trial groups was detected and shown in Table 3. However, the concentration was different in all the groups. The filler contents showed almost similar elemental composition and concentration.

|       | C   | O   | Zr  | Ba  | F   |
|-------|-----|-----|-----|-----|-----|
| G0    | 52.59 | 26.59 | 3.88 | 14.91 | 2.03 |
| G20   | 55.04 | 27.67 | 2.63 | 13.36 | 1.30 |
| G40   | 56.14 | 27.86 | 2.22 | 12.72 | 1.06 |

![Figs 3A to C: FESEM: (A) G0; (B) G20; (C) G40](image)
Composite with Dipentaerythritol Penta-/Hexaacrylate

The Journal of Contemporary Dental Practice, Volume 22 Issue 6 (June 2021)

unreacted aliphatic C–C. The Abs peak at 1638 cm\(^{-1}\) surprisingly vanished in the polymerized specimens of both trial groups, which is inferred as less or negligible residual monomer. However, for the polymerized specimens of the G0, a weak Abs peak around 1638 cm\(^{-1}\) confirms the existence of unreacted residual monomer.

Table 4 presents the medians of the groups and shows significant differences among the groups (\(p = 0.000\)). Table 5 shows a statistically significant difference between the groups (\(p = 0.000\)) by multiple comparisons. The DC of trial groups was greater than the control group. The DC of G40 was greater than the G20.

Glass Transition Temperature

The mean (SD) \(T_g\) (°C) of G0, G20, and G40 groups was 59.53 (0.72), 67.11 (1.06), and 81.50 (0.44), respectively. Significant differences were evident among and between the groups (\(p = 0.000\)). The \(T_g\) of trial groups was greater than the control. The \(T_g\) of G40 was higher than the G20. Hence, the addition of DPEPHA increased the \(T_g\) of the new copolymer P(GEU-Co-DPEPHA). Figure 5 illustrates the DSC curves of the groups.

Discussion

The effect of copolymerization caused by the addition of the DPEPHA comonomer on the DC and \(T_g\) of photo-polymerizable dental restorative composite material was demonstrated in this research. To build the novel P(GEU-Co-DPEPHA) copolymer, the composition of the GEU-based composite resin was chemically changed by adding DPEPHA (20 and 40 wt.%). In the trial groups, peaks at 810.01 cm\(^{-1}\) attributable to C–H bending of multi-substituted acrylate moiety in the FTIR spectra, additional protons attributable to (\(\text{–C–CH}_2\text{–O–CH}_2\text{–C}\)), (\(\text{–CH}_3\text{–CH=O–CH}_2\text{–C}\)), and additional C-atoms attributable to (\(\text{–C–CH}_2\text{–O–CH}_2\text{–C}\)), (\(\text{–CH}_3\text{–CH=O–CH}_2\text{–C}\)), (\(\text{–CH}_2\text{–C}\)) attached to acrylate moiety in the NMR spectroscopies asserted the formation of the new copolymer P(GEU-Co-DPEPHA). Furthermore, this was corroborated with EDX spectroscopy, demonstrating higher C mass% in trial groups than the control.

Chroszcz and Barszczewska-Rybarek\(^{33}\) developed a novel urethane dimethacrylate monomer with two quaternary ammonium groups and used FTIR-ATR and NMR spectroscopies to

Degree of Conversion

Figure 4 shows Abs peaks at 1638 cm\(^{-1}\) and 1608 cm\(^{-1}\) for unpolymerized specimens in all the groups, which correspond to
validate the chemical structure. FTIR-ATR and NMR spectroscopies were used by Al-Odayni et al. to validate the synthesized chlorinated bis-GMA. When compared to bis-GMA, chlorinated bis-GMA displayed stronger DC. FTIR, 1H-NMR, 13C-NMR, and EDX spectroscopies, as well as EDX spectroscopy, were used to ascertain the P(GEU-Co-DPEPHA) copolymer formation in this research.

The DC in the trial groups was higher than in the G0 group. Reactive moieties are responsible for the rate of conversion. For faster reaction kinetics, the acrylic moieties of multifunctional acrylates (DPEPHA) are used instead of the methacrylic moieties of propriety dimethacrylates. The second pendant methacrylate group is prognosticated to be 7.5–10 times less reactive after the first methacrylate group has reacted in dimethacrylates. As a result, the final conversion during polymerization is reduced. The acrylic moieties with rapid reaction kinetics in DPEPHA, on the other hand, resulted in increased conversion and in turn decreasing the residual monomer content. The Abs peak at 1638 cm\(^{-1}\) in the FTIR spectra correlates with the presence of unreacted residual monomer (C=O). The absence of the Abs peak at 1638 cm\(^{-1}\) for the P(GEU-Co-DPEPHA) copolymer in this research indicates that it has a higher DC and less residual monomer than the G0.

The flexibility of the monomers can be calculated using viscosity or \(T_g\), and there has previously been a strong correlation found between bis-GMA concentration and \(T_g\) as well as \(T_g\) and DC in bis-GMA/TEGDMA systems. To ensure the longevity of a dental restoration, the \(T_g\) of polymeric resins suggested for use as new restorative materials must be taken into account. The \(T_g\) of the oligomeric and DPEPHA-prepared specimens is substantially different, meaning that the structure of the polymer was influenced by the pre-reaction. The difference in \(T_g\) between the groups is due to a decrease in allyl co-/homopolymerization in the G0, which results in a lower cross-linking density. Furthermore, although the trial groups tested here all had a high \(T_g\), P(GEU-Co-DPEPHA) had better polymer homogeneity, as demonstrated by a narrow glass transition range that was unaffected by oligomerization or copolymerization.

DPEPHA was substituted in the GEU resin matrix at concentrations of 20 wt.% and 40 wt.% in this research. DPEPHA’s copolymerizing ability with GEU resin matrix monomers, DC, and \(T_g\) greater than 40 wt.% has yet to be tested. Since this is the only analysis of DPEPHA in a restorative composite resin, the findings should be viewed with caution. More studies should be done to see how increasing the concentration of DPEPHA affects mechanical properties and biocompatibility.

**Conclusion**

It can be concluded that there was a firm authentication of copolymerization of DPEPHA comonomer with the propriety GEU resin matrix. Surface topography appeared homogenous and smooth along with high C wt% in P(GEU-Co-DPEPHA) copolymer. The DC and \(T_g\) were augmented with the inclusion of DPEPHA in the propriety GEU resin matrix. The P(GEU-Co-DPEPHA) copolymer with 40 wt.% DPEPHA had the highest conversion and \(T_g\).

**Clinical Significance**

The analysis of copolymerization in dental restorative composite resin by adding a comonomer offers a modification or reinforcement process that is intended to enhance the material’s mechanical properties and biocompatibility. As a result, the efficiency and reliability of the restoration will increase, giving the affected population a better quality of life.

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