Effect of novel cycloaliphatic comonomer on the flexural and impact strength of heat-cure denture base resin

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Materials and Methods

Heat-cure denture base acrylic resin (DPI Heat Cure; Dental Products India, Mumbai, India) and the cycloaliphatic monomer TCDDMDA (Sigma-Aldrich, St. Louis, MO, USA) were chosen for this research (Table 1). The control (C) PMMA specimens for FS and IS experiments were prepared from 100% MMA monomer and the control groups were designated.
Table 1. Materials used in this study

| Material                          | Manufacturer                              | Batch lot number | Composition                                                                 |
|----------------------------------|--------------------------------------------|------------------|-----------------------------------------------------------------------------|
| Heat-cure denture base acrylic resin | DPI Heat Cure, Dental Products of India, Mumbai, India | Polymer: 1184 Monomer: 1186 | Powder: includes polymerized heads of poly(methyl methacrylate), benzoyl peroxide as the initiator, dibutyl phthalate as plasticizer and pigments |
| Tricyclodecane dimethanol diacrylate (TCDDMDA) | Sigma-Aldrich, St. Louis, MO, USA | MKCG3853 CAS no. 42594-17-2 | Monomer: includes methyl methacrylate, dibutyl phthalate, ethylene glycol dimethacrylate as the cross-linker, and hydroquinone as the inhibitor |

Table 2. Specimen distribution

| Flexural strength (n = 75) | Impact strength (n = 75) |
|---------------------------|-------------------------|
| Control groups: PMMA specimens with 100% MMA |
| Group-FS (n = 25) | Group-IS (n = 25) |
| Experimental groups: PMMA specimens with 10% and 20% TCDDMDA |
| Group-FS10 (n = 25) | Group-IS10 (n = 25) |
| Group-FS20 (n = 25) | Group-IS20 (n = 25) |

Table 3. Comparison of median (IQR) flexural strength among groups

| Group | Flexural strength (MPa) | Test value | P-value |
|-------|-------------------------|------------|---------|
| FSC   | 36.0 (12.0)             |            |         |
| FS10  | 72.0 (12.0)             | 66.826     | 0.000*  |
| FS20  | 108.0 (6.0)             |            |         |
| ISC   | 36.0 (12.0)             |            |         |
| IS10  | 50.0 (12.5)             | 63.757     | 0.000*  |
| IS20  | 62.5 (12.5)             |            |         |

*Asymptotic significances are displayed. The significance level is 0.05.

Table 4. Comparison of the median (IQR) impact strength among groups

| Group | Impact strength (kJ/m²) | Test value | P-value |
|-------|-------------------------|------------|---------|
| ISC   | 25.0 (12.5)             |            |         |
| IS10  | 50.0 (12.5)             | 63.757     | 0.000*  |
| IS20  | 62.5 (12.5)             |            |         |

*Asymptotic significances are displayed. The significance level is 0.05.

as FSC and ISC respectively. The experimental P(MMA-Co-TCDDMDA) copolymeric specimens for FS and IS experiments were prepared from a monomer mixture containing 10% (v/v) TCDDMDA comonomer in MMA monomer. The experimental groups of FS and IS experiments were designated as FS10 and IS10 respectively. Likewise, the experimental groups FS20 and IS20 consist of copolymeric specimens prepared from a monomer mixture containing 20% (v/v) TCDDMDA comonomer in MMA monomer. Table 2 describes the distribution of specimens in the groups for FS and IS. The pre-prepared monomers were stored in three individual identical dark glass containers and labeled with notes about the appropriate concentrations. Author blinding was accomplished by concealing the labels with opaque stickers with random numbers from one to three (M1, M2, and M3) to avoid an expectation bias.

Seventy-five PMMA specimens (65 × 10 × 2.5 mm³) [13] for FS and seventy-five specimens (80 × 10 × 4 mm³) [14-17] for IS were prepared out of dies, laser-cut from commercially available acrylic sheets. Dies were impressed into putty impression material (Photosil soft putty; DPI, Mumbai, India) within the dental flask to obtain a mold space. According to the manufacturer’s instructions, the polymer was mixed with the monomer in 3:1 ratio and packed into mold space in the dough stage at a packing pressure of 3,500 psi via a mechanical press (Sirio Dental Srl, Meldola, Italy) for 10 min. The dough-forming time was 8 min for the control group and 15 min for the experimental groups. The heat-cure cycle included exposure at 74°C for 8 h, followed by terminal boiling treatment at 100°C for 1 h in an acrylizer (Unident Instruments Pvt. Ltd., New Delhi, India). The unnotched specimens [14,17,20] were supported 10 mm from the edges on each side and flatwise so that the impact span length was 60 mm [16]. The pendulum of the testing machine used in this research has an impact capacity of 164 J and a striking velocity of 5.6 m/s. Initially, the pendulum was dropped from a specific height to record the zero reading (zeroing). Then, the specimens were placed flatwise, and the pendulum was dropped again to impact the specimen. The energy absorbed by the material was obtained by the difference between these reading values (corrected reading) [20]. Charpy’s IS was measured in kJ/m² by applying the following equation: IS = CR / A, where CR is the corrected reading in kJ and A is the test specimen area (breadth × thickness) in m².

Statistical analysis

All analysis was conducted using the Statistical Package for the Social Sciences (SPSS) version 20.0 software program (SPSS Inc., Chicago, IL, USA). Descriptive statistics were performed. Lilliefors significance correction by the Kolmogorov-Smirnov test of normality showed that there was a statistically significant difference apparent within the data distribution among each group of both FS and IS. Based on data distribution, continuous data were presented as median and quartiles. Separately, the nonparametric Kruskal-Wallis test was carried out to analyze differences in the mechanical properties between the control and test specimens. Post hoc multiple pairwise comparisons were conducted by Dunn’s test (α = 0.05). A P-value of less than 0.05 was considered to indicate statistical significance.

Results

Tables 3 and 4 show the median (+ interquartile range [IQR]) FS and IS of the compared groups, respectively. Group FS20 (108.0 ± 6.0 MPa) possessed a greater FS when compared with FS10 (72.0 ± 12.0 MPa). The FS was smallest in the control group FSC (36.0 ± 12.0 MPa). Group IS20 (62.5 ± 12.5 kJ/m²) possessed a greater IS than that of IS10 (50.0 ± 12.5 kJ/m²). The IS was smallest in the control group ISC (25.0 ± 12.5 kJ/m²). There exists a statistically significant difference existed between the groups of both FS and IS (P < 0.05). Greater FS and IS values were found among the experimental specimens when compared with the control specimens. Both the FS and IS were increased by the addition of TCDDMDA comonomer to MMA.

Discussion

Monomer modifications of denture base acrylic resins are not uncommon. Numerous researches have explored the use of monomer modifications to improve the physicomechanical properties of denture base resins [10]. TCDDMDA is a novel cross-linking, difunctional, dual-reactive, cycloaliphatic acrylic monomer. In their report, Ajay et al. [11,12] suggested that TCDDMDA comonomer can easily copolymerize with PMMA and is noncytotoxic to the mouse fibroblast. However, there appear to be no studies that have assessed the influence of this novel monomer on FS and IS. In the present study, the addition of TCDDMDA comonomer to MMA increased both the FS and IS of denture base resin. Hence, the null hypoth-
Table 5: Post hoc Dunn’s test of FS

| Group comparison | Test statistic | Standard error | Standard test statistic | P-value |
|------------------|----------------|----------------|-------------------------|---------|
| FSC-FS10         | −25.000        | 6.116          | −4.087                  | 0.000** |
| FSC-FS20         | −50.000        | 6.116          | −8.175                  | 0.000** |
| FS10-FS20        | −25.000        | 6.116          | −4.087                  | 0.000** |

**Asymptotic significances (two-sided tests) are displayed. The significance level is 0.05.**

Table 6: Post hoc Dunn’s test of IS

| Group comparison | Test statistic | Standard error | Standard test statistic | P-value |
|------------------|----------------|----------------|-------------------------|---------|
| ISC-IS10         | −27.080        | 6.018          | −4.500                  | 0.000** |
| ISC-IS20         | −47.920        | 6.018          | −7.962                  | 0.000** |
| IS10-IS20        | −20.840        | 6.018          | −3.463                  | 0.001** |

**Asymptotic significances (two-sided tests) are displayed. The significance level is 0.05.**

Asymptotic significances (two-sided tests) are displayed. The significance level is 0.05.

The observed increase in FS can be attributed to reactive moieties. The acrylic moieties of diacrylates are generally more reactive than the methacrylic moieties of dimethacrylates and are thus relied upon when faster reaction kinetics are desired. In the context of dimethacrylate cross-linkers, after the first methacrylate group has reacted, the second pendant methacrylate group is estimated to be less reactive by 7.5- to 10-fold. The final conversion for copolymerization of MMA with ethylene glycol dimethacrylate (EGDMA) decreases together with the increasing content of this cross-linking agent. Such pendant dimethacrylate groups in control specimens acted as plasticizers at low deformation rates and were responsible for the lower FS than that found in the experimental groups. This plasticizing effect is due to the pendant methacrylate groups that separate the main chain segments [21].

TCDDMDA is a cycloaliphatic cross-linker possessing a tri-ring central structure and no (CH\text{2}-O) units in cross-linkers. Ruyter and Svendsen [21] suggested that differences in FS can be inferred by comparing the composition of monomer liquids. Monomers encompassing the cross-linking agent 1,4-butanediol dimethacrylate had a higher FS than that of EGDMA. Hence, from the above evidence, it is clear that the cross-linker’s concentration, chain length, and type determine the FS of denture base resins.

With respect to IS, the addition of TCDDMDA comonomer to MMA increased the IS of denture base resin and was higher for IS10 and IS20 groups than the ISC group. This was in accordance with research performed by Al-Husayni and Hatoor [15], who substituted silver nitrate solution in MMA and concluded that silver nitrate at 60 ppm showed a higher IS than did the control. In contrast, the IS was decreased with the addition of dimethyl itaconate and di-n-butyl itaconate in MMA [16]. However, the addition of ethylene glycol methacrylate phosphate [34] and di-tetra hydrofurfuryl itaconate [35] in MMA did not adversely affect the IS of acrylic resin. As stated above, IS is also affected by the reactive moieties, concentration of the cross-linker, and type of the cross-linker used.

Notching the specimens is not uncommon and is normally performed in impact testing. However, the methods used to apply the notch can induce unique stresses and can be difficult, time-consuming, and nonreproducible to complete [36]. The currently used test specimens were unnotched because a better correlation was found between the IS and the energy absorbed in a flexural test with unnotched test specimens [37]. Al-Mulla et al. [38] compared the IS of notched and unnotched PMMA materials and observed the same ranking order, irrespective of specimen preparations. Hence, in the present in vitro study, unnotched specimens were tested for IS.

The present investigation was a triple-blinded study. The author, operator, and statistician were blinded by concealing the concentration of TCDDMDA comonomer substituted in MMA to avoid the creep of an expectation bias into the result. This study has limitations, and the results should be interpreted with caution. For example, although the specimens were immersed in water at 37°C to simulate the clinical situation, in adverse oral environment conditions, the materials are also submitted to thermal and loading stresses, and these aspects should be considered in future studies. This is the only research conducted concerning the FS and IS with TCDDMDA. Hence, the results must be carefully interpreted and extrapolated. Future investigations are necessary to evaluate the effect of TCDDMDA comonomer at a concentration of more than 20% by weight on the mechanical properties with mechanical loading and thermocycling.

In conclusion, within the limitations of this study, the addition of TCDDMDA comonomer to MMA increased both the FS and IS of heat-cure denture base resin. Meanwhile, more specifically, the addition of 20% TCDDMDA comonomer in MMA showed the highest FS and IS.

Conflict of interest
None.

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