ORIGINAL RESEARCH

Chemical Characterization and Degree of Conversion of a Novel Denture Base Polymer Processed by a Novel Photon-thermal Dual Polymerization Technique

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Abstract

Aims and objectives: The present research aimed to characterize the thermo-polymerized poly(methyl methacrylate) [TP-P(MMA)] with camphorquinone-2-(dimethylamino)ethyl methacrylate (CQ-DMAEMA) complex and to evaluate the degree of conversion (DC) of the formed novel copolymer P(MMA-*co*-DMAEMA).

Materials and methods: The CQ was incorporated in the prepolymeric powder and the DMAEMA in the liquid monomer so that the CQ-DMAEMA ratio was 1:2. The CQ-DMAEMA complex concentration in the TP-P(MMA) was 5% (group B), 10% (group C), and 15% (group D). The TP-P(MMA) without the CQ-DMAEMA complex served as control (group A). Ten polymerized and unpolymerized specimens (n = 10 per group) were subjected to Fourier transform infrared spectroscopy (FTIR) using potassium bromide technique for assessing the copolymerization (CP) and DC.

Results: New peaks ascribed to the methyl amino and tertiary amine groups were evident in all the trial groups which were absent in the control group. These peaks of the trial groups confirm the CP of the methacrylated amine with TP-P(MMA). Absence of the alkenyl C=C stretch peak in all the trial groups signifies higher DC than the control group. The TP-P(MMA) with 15% CQ-DMAEMA complex had the highest DC.

Conclusion: The methacrylated amine successfully copolymerized with TP-P(MMA) which along with CQ formed a novel photon-thermal dual polymerized denture base copolymer P(MMA-*co*-DMAEMA) exhibiting higher DC than the conventional P(MMA).

Clinical significance: The novel photon-thermal dual-polymerized denture base copolymer possessing good DC is expected to release meager or negligible amount of unreacted residual monomer and would possess palatable biocompatibility than the conventional P(MMA) without inducing denture-induced stomatitis in the edentulous geriatric population.

Keywords: Camphorquinone, Co-initiator, Copolymer, Denture base resin, Dual-cure.

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Introduction

Acrylic denture base resin (DBR) was introduced in dentistry in the early 1930s and employed in routine dental practice owing to its palatable properties and indispensable features for its utility in myriad functions. The P(MMA)-based acrylic resins are used in the construction of various intra/extraoral prostheses, videlicet temporary crowns/bridges, removable orthodontic appliances, removable denture bases, and overdentures that are used to rehabilitate the vanishing hard and soft tissues and direct occlusal forces from the denture to the underlying stress-bearing regions of the edentulous arches.[1]

Different approaches for activating polymerization are chemical, photonic, and thermal or microwave energy, that yields a multiphase polymer. In radical initiated polymerization, the DC is never complete, and approximately 0.2–0.5% unpolymerized monomer (UM) persists in the TP DBR.[2] The UM and its other obnoxious metabolic byproducts like formaldehyde, methacrylic acid, benzoic acid, phenyl benzoate/salicylate, and leached-out plasticizer crop up on the denture surface due to inadequate DC.[3] These offensive substances formed in the polymeric network lead to *in vitro* cytotoxicity and *in vivo* hypersensitivity reactions.[1] Cytotoxic impacts of DBR are ascribed to polymer–monomer proportion, water immersion time, and polymerization strategy. Polymer degradation does not happen in secluded events, as multifarious components such as saliva, oral microorganisms, and chewing force are considered liable for biodegradation.[4,5] Salivary esterases demonstrate esterification of polymeric side chains that eventually led to compromised surface properties. It seldom is inferred that the polymerization by thermal activation completely eschews the UM release.[6–8]

To steer clear of these pitfalls, myriad powder and monomeric modifications/substitutions have been studied extensively.[9] The CQ (1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-dione), an aliphatic α-diketones photoinitiator, has been employed in the free radical addition polymerization of the resin monomers.[10] Photopolymerization utilizes a light source to cleave CQ into free radicals, which interact with reactive terminals (C=C bonds) in

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the monomers or prepolymers, leading to photo-cross-linkage.[11] A novel attempt to incorporate CQ in P(MMA) prepolymeric powder would lead to the development of a novel photon-thermal dual-polymerized DBR, where the resinous dough would be polymerized by both heat and light. The polymerization rate would be amplified by a tertiary amine as a co-initiator enhancing the photon absorption efficiency. The DMAEMA is a generally used methacrylated amine co-initiator that acts as a source of electrons for charge transfer during the initiation cycle.[12]

However, the addition of the CQ-DMAEMA complex in TP-P(MMA) and its impact on the DBR's properties are not yet reported. It is customary to characterize a dental material with a novel additive/substitute. The CP can be evaluated while characterizing the material as it decides the physico-mechanical properties of a material. The FTIR is one of the most commonly used and grounded techniques for analyzing and characterizing the structure of resultant polymers/copolymers.[13] The present research aimed to characterize the TP-P(MMA) with the CQ-DMAEMA complex and to evaluate the DC using FTIR spectroscopy. The null hypothesis of this research is that the addition of the CQ-DMAEMA complex in TP-P(MMA) could have no effect on the DC if the CP is evident.

Materials and Methods

The materials used in the current research were tabulated in Table 1. The modification of the prepolymeric powder was executed by incorporating CQ (Fig. 1A) at appropriate concentrations. The monomer modification was done by pipetting an appropriate quantity of DMAEMA (Fig. 1B) in the MMA. The total CQ-DMAEMA ratio in a TP specimen was 1:2. The modified polymer and monomer were stored in four identical dark containers and labeled with appropriate concentrations. Random numbered opaque stickers were used to conceal the labels. The principal investigator was blinded to avoid experimental bias. The CQ-DMAEMA complex concentration in the TP-P(MMA) was 5% (group B), 10% (group C), and 15% (group D). The TP-P(MMA) without the CQ-DMAEMA complex served as control (group A).

Metallic dies (25 mm diameter and 3 mm thickness) were invested in a dental flask using type IV die stone to obtain mold space for fabricating polymerized trial and control specimens. Prepolymeric powder and monomer were mixed in a 3:1 ratio, and the dough was trial packed separated by a cellophane sheet in a mechanical press (Sirio; Dental Metal Hydraulic Press, Gujarat) at 1500 psi. For the trial groups, the flasks were opened, and excess flash material was removed. Then the flasks were immediately placed in the light-cure chamber and photopolymerized for 40 seconds (Sibari SR620; Sirio Dental Division, Meldola, Italy) (Fig. 2). This step was eschewed for the control group. Finally, the flasks were pressed at 3500 psi for 20 minutes and TP for 8 hours at 74°C with terminal boiling for half an hour in an automated water bath [Unident Instruments (India) Pvt. Ltd.]. The cooled flasks were deflasked, and the specimens were recovered, finished, and cleansed. Ten polymerized specimens ($n = 10$) for each group were concocted by a lone investigator and stored in distilled water for 24 hours at 37 (±1)°C. The groups and the composition of the specimens in each group were tabulated in Table 2.

Table 1: Materials and manufacturer

Material	*Lot/Batch no.*	*Manufacturer/Supplier*
TP-P(MMA)	Powder: YT0306 Liquid: Y36242	Ivoclar Vivadent AG, Schaan, Liechtenstein
CQ	09003AQV	Sigma Aldrich Co., St. Louis, Missouri, USA
DMAEMA	BCCB1321	

FTIR Spectroscopy and DC

The CP and DC were determined by FTIR (ThermoScientific™ Nicolet™ iS™5; iD1 Transmission, Waltham, Massachusetts, USA) spectroscopy at transmittance and absorbance (Abs) mode, respectively. Both polymerized ($n = 10$ for each group) and unpolymerized material ($n = 10$ for each group) were investigated for DC. The unpolymerized specimens were prepared and subjected to infrared spectroscopy by following the technique elucidated elsewhere.[14] The laboratory technician was blinded by the composition of the specimen. The DC was calculated utilizing the formula:

$$DC\% = \left[1 - \frac{\left(\frac{Abs1638}{Abs1720}\right)_{Polymerized}}{\left(\frac{Abs1638}{Abs1720}\right)_{Unpolymerized}}\right] \times 100$$

where Abs1638 and Abs1720 correspond to the intensities of the aliphatic double bonds and the carbonyl peaks, respectively.



Figs 1A and B: (A) Camphorquinone; (B) 2-(Dimethylamino)ethyl methacrylate



Fig. 2: Specimens in the light-cure chamber

Statistical Analysis

The data were entered in Microsoft Excel spreadsheet and analyzed using Statistical Package for the Social Sciences (SPSS) software version 21.0. Normality of the data was tested using Shapiro–Wilk test. Descriptive statistics were done. One-way analysis of variance (ANOVA) and *post hoc* Bonferroni multiple comparison tests were used to compare the DC between the groups. $p < 0.05$ was considered for statistical significance.

Table 2: Groups and specimens' composition

Group		*Composition*
Control	A	Powder: 75 gm of prepolymeric powder Liquid: 25 mL of MMA
Trial	B	Powder: 73.35 gm of prepolymeric powder + 1.65 gm of CQ Liquid: 21.65 mL of MMA + 3.35 mL of DMAEMA. The concentration of CQ-DMAEMA complex is 5%
	C	Powder: 71.67 gm of prepolymeric powder + 3.33 gm of CQ Liquid: 18.33 mL of MMA + 6.67 mL of DMAEMA. The concentration of CQ-DMAEMA complex is 10%
	D	Powder: 70 gm of prepolymeric powder + 5 gm of CQ Liquid: 15 mL of MMA + 10 mL of DMAEMA. The concentration of CQ-DMAEMA complex is 15%

Results

FTIR Spectroscopy

The FTIR spectra of the trial groups B, C, and D differed from the control by the appearance of new peaks at 2846.89 cm^{-1}, 2846.41 cm^{-1}, and 2846.81 cm^{-1}, respectively, which is attributed to the methyl amino $–N(CH_3)_2$ and (C–H) stretch (zone I). The peak present in the control group at 1638.75 cm^{-1} attributed to aliphatic C=C stretch absent in the trial groups (zone II). The presence of new peaks in group B (1272.78 cm^{-1}, 1241.93 cm^{-1}, and 1146.95 cm^{-1}), group C (1273.27 cm^{-1}, 1240.00 cm^{-1}, and 1145.95 cm^{-1}), and group D (1272.78 cm^{-1}, 1241.45 cm^{-1}, 1145.99 cm^{-1}) that are attributed to the tertiary amine stretch (C–N) is absent in control group (zone III). In zone IV, *trans*-(C–H) wagging peak is seen in the control group at 989.30 cm^{-1} and gets less intensified in trial groups. The presence of a peak attributable to CH_2 wagging in the control group did not appear in the trial groups. The peak intensities of the vinylidene (C=C) bend and *cis*-(C–H) wagging in the control group diminished in group B and disappeared in groups C and D. The appearance of these new peaks confirms CP and novel copolymer P(MMA-*co*-DMAEMA) configuration. Table 3 tabulates the functional groups and their corresponding wave numbers of all the groups. Figure 3 illustrates consolidated FTIR spectra with the differences highlighted in the corresponding zones.

Degree of Conversion

The mean and standard deviation (SD) of the groups were tabulated in Table 4. A significant difference among the groups ($p = 0.0001$) was observed. The DC of the control was lesser than the trial group. Among the trial groups, group D exhibited maximum conversion, followed by group C and group B. Table 5 shows the

Table 3: FTIR spectra of polymerized specimens

	Wave numbers (cm^{-1}); peak intensity				
		Trial groups			
Functional groups: attributions	*Group A (control)*	*B*	*C*	*D*	*Zone*
O–H stretch of physisorbed moisture	3498.23	3435.56	3436.04	3435.56	
CH_3 stretch (C–H)	2995.87	2996.83	2996.83	2995.87	
Aliphatic chain $–CH_2–$ stretch (C–H)	2951.03	2951.51	2951.51	2951.51	
Methyl amino $–N(CH_3)_2$ and (C–H) stretchs	Absent	2846.89	2846.41	2846.81	I
Carbonyl stretch (C=O)	1726.46	1725.97	1725.49	1725.01	
Aliphatic carbon–carbon (C=C) stretch	1638.75	Absent	Absent	Absent	II
CH_2 asymmetric bend (C–H)	1482.99	1482.02	1482.02	1481.54	
CH_3 asymmetric bend (C–H)	1449.24	1448.76	1448.76	1448.27	
CH_3 α-methyl bend ($C–CH_3$)	1386.56	1386.56	1386.08	1386.08	
Tertiary amine stretch (C–N)	Absent	1272.78, 1241.93, 1146.95	1273.27, 1240.00, 1145.99	1272.78, 1241.45, 1145.99	III
Aliphatic ether linkage I stretch ($–C–O–CH_2–$)	1194.20	1194.20	1194.68	1194.20	
Trans-(C–H) wagging	989.30	989.78	1001.35	1007.14	
CH_2 wagging	912.64	Absent	Absent	Absent	IV
Vinylidene (C=C) bend	841.29	851.90	Absent	Absent	
Cis-(C–H) wagging	751.61	765.60	Absent	Absent	

Bonferroni multiple comparisons between the groups. All the comparisons exhibited statistically significant differences ($p = 0.000$). Figure 4 shows the FTIR graphs depicting the peak intensity differences between polymerized and unpolymerized specimens.

Discussion

Four spectral differences are observed among the groups. First difference is the appearance of a new peak attributable to the methyl amino $-N(CH_3)_2$ and (C–H) stretch in all the trial groups and the absence of this peculiar peak in the control group. Second difference is the appearance of new peaks attributable to C–N (–N=; tertiary nitrogen) stretch in all the trial groups, which are absent in the control group. These differences apparently flash the absence of tertiary amine in the control group and prove the incorporation of DMAEMA by the presence of the peak corresponding to tertiary amine in the trial groups. The abovementioned new peaks were approximately the same and in accordance with the FTIR spectrum of P(DMAEMA) obtained by Stawski and Nowak.[15]

Ajay et al.[16] copolymerized cycloaliphatic tricyclodecane dimethanol diacrylate (TCDDMDA) comonomer with the MMA. The manifestation of peak at 1386.56 cm^{-1} affirmed the configuration of a novel denture copolymer. Ajay et al.[17] also copolymerized 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5,5]undecane (DMTOSU) with the TP-P(MMA). The presence of aliphatic ether linkage peaks ($C–O–CH_2$ at 1202 cm^{-1} and $CH_2–O–CH_2$ at 1149 cm^{-1}) and the absence of tetraoxaspiro linkage peak confirmed the ring-opening of DMTOSU and formation of the copolymer. Rodriguez et al.[18] affirmed the CP of amine-containing methacrylate comonomer with TP-P(MMA). The new Abs peaks in trial groups were affiliated with secondary amine (–NH–), which were absent in the control group. Al-Ali and Kassab-Bashi[13] affirmed the CP by subbing three acrylate-based comonomers in MMA. Spasojevic et al.[19] successfully copolymerized itaconate comonomers with P(MMA). Therefore, from the above context, it is apparent that MMA can readily copolymerize with multitude monomers.

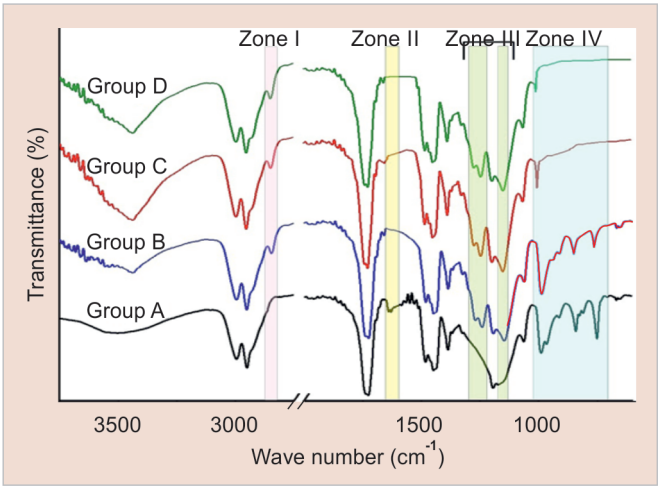

Fig. 3: Consolidated FTIR spectra of all groups

Table 4: One-way ANOVA of DC

Group	*Mean ± SD*	*f-ratio*	*p-value*
A	76.93 ± 0.48	3304.90326	0.0001
B	82.35 ± 0.42		
C	88.99 ± 0.19		
D	90.00 ± 0.12		

Besides the three-dimensional polymeric network, the DC is of prime concern in the field of dentistry because it influences the biomaterials' properties and biocompatibility. There is an inverse relationship between DC and the amount of unpolymerized (C=C) monomers.[20] The existence of unpolymerized residual C=C bond in the control group could be due to incomplete conversion. Nevertheless, the final DC relies upon the chemical structure of comonomer substituted, polymerizing temperature and time, and operating room ambients.[21] The DC of C=C bonds, for the most part, falls in the range of 55–65%.[22] However, this does not imply that 35–45% of monomers are unpolymerized. In actuality, it implies that 35–45% of the C=C bonds did not participate in polymerization. It is conceivable that dimethacrylates possessing two-terminal C=C bonds might interact with one of the single terminal C=C double bonds, with the second being uninvolved in polymerization reaction. The second pendant [$H_2C=C(CH_3)C(O)O$] group is 7.5–10 times less reactive after the first [$H_2C=C(CH_3)C(O)O$] group gets initiated by the free radical and reacts.[23] This is the reason attributed to decreased final DC. However, this is not a problem because DMAEMA is a monomethacrylate as much as MMA.

In the present research, the third distinction is the absence of C=C peak in the trial groups. Though the monomer–polymer conversion is seldom absolute, the peak absence could be attributed to polymerization with subtotal monomer–polymer conversion. This can be attributed to the presence of two distinct initiators. Dibenzoyl peroxide (DBPO) is a type-I initiator initiating the polymerization by α-cleavage, and CQ is a type-II initiator initiating the polymerization by H-abstraction. Hence, both the initiators yield free radicals independently once activated. A part conversion occurred when the specimens were subjected to photopolymerization, and the balance conversion was taken care of by thermo-polymerization shortly thereafter. Thus, the photon-thermal dual polymerization greatly increased the DC

Table 5: Bonferroni multiple comparisons of DC

Group (I)	*Group (J)*	*Mean difference (I – J)*	*Std. error*	*Sig.*	*95% confidence interval*	
					Lower bound	*Upper bound*
A	B	–5.42200*	0.15061	0.000	–5.8425	–5.0015
	C	–12.06600*	0.15061	0.000	–12.4865	–11.6455
	D	–13.07800*	0.15061	0.000	–13.4985	–12.6575
B	C	–6.64400*	0.15061	0.000	–7.0645	–6.2235
	D	–7.65600*	0.15061	0.000	–8.0765	–7.2355
C	D	–1.01200*	0.15061	0.000	–1.4325	–0.5915

*The mean difference is significant at the 0.05 level

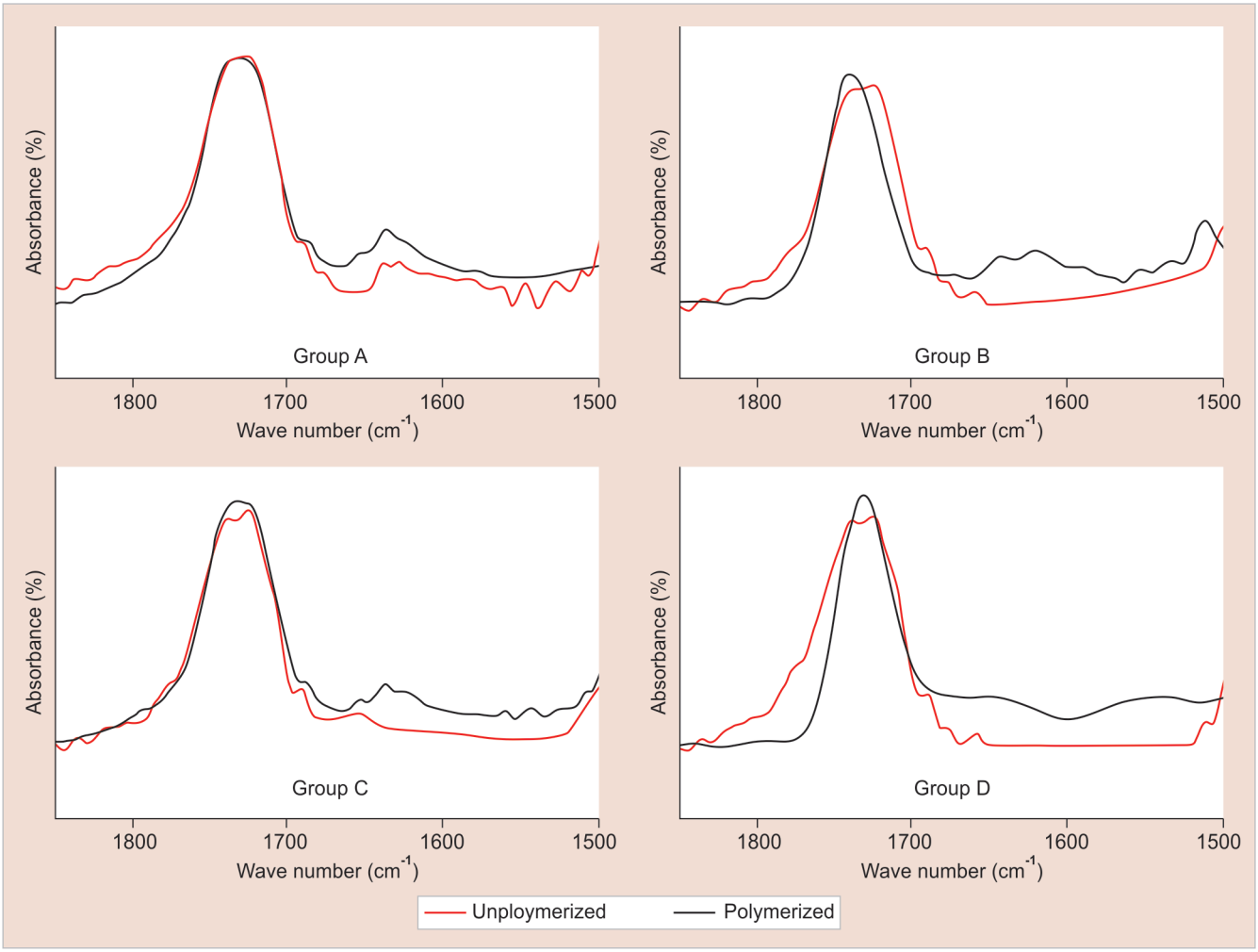

Fig. 4: IR graphs depicting the DC of all groups

of the trial groups, and a maximum DC was observed when the CQ-DMAEMA complex's concentration was 15%.

Al-Ali and Kassab-Bashi[13] reported no C=C transmittance peak in the FTIR spectra upon subbing acrylate-based comonomers in MMA. The disappearance of C=C peak was also demonstrated by Ajay et al. when substituting TCDDMDA and DMTOSU as comonomers in TP-P(MMA).[16,17] Hence, from the above context, it is inferred that this disappearance of C=C peak is suggestive of high DC. The result of the present research is in line with these previous researches. The fourth difference in the FTIR spectra of groups C and D is the absence of peaks affiliated to vinylidene (C=C) bend and *cis*-(C–H) wagging and the appearance of these rather fewer intensity peaks in group B. Thus, group B exhibits lesser DC than groups C and D. The same peak affiliations were even more accentuated in the control group A. Therefore, the ascending order of the DC is group A < group B < group C < group D. Hence, the null hypothesis was rejected.

Although CQ can release free radicals by itself upon photoinitiation, it is less effective without a co-initiator. The emission spectrum of a light source is the pivotal factor to be considered for effective excitation of CQ particles. The CQ triplet exciplex (CQE) formation time is critical due to the extremely short half-life of CQE (~0.05 seconds). The free radical formation ceases after half-life because the CQE decay to its primary condition.[24] The polymerization effectiveness relies upon the steric configuration of radicals emancipated from amine-based co-initiators.[25,26] The routinely employed co-initiators are aromatic tertiary amines.[26,27] *N*,*N*-dimethyl-*p*-toluidine is found to be a noxious co-initiator because of its low atomic mass. Likewise, ethyl-4-(dimethylamino) benzoate (EDMAB) also exhibits cytotoxic reactions since it cannot copolymerize with propriety monomers and enhances intracellular oxidants formation and eventually increases the cellular glutathione level, which can sever DNA coherence.[28,29] The DMAEMA demonstrates the best biocompatible properties that do not leach out.[30] This can be attributed to the fact that the DMAEMA participates in the polymerization reaction through the methacrylate functional moiety. The aromatic amines possess better hydrogen donor capability and electron localization, permitting electron relocation and decreasing the chance of back electron relocation than the linear chain amines. The phenomenon of back electron relocation hinders H-abstraction and represses polymerization.[27] However, Schroeder and Vallo[31] reported that though the DMAEMA has a lower co-initiating effect than the EDMAB, it is the most biocompatible amine co-initiator. Hence, in the present research, DMAEMA was employed as the co-initiator, which successfully copolymerized with MMA.

Incorporating the CQ-DMAEMA complex in P(MMA) was a theoretical conception based on the existing dual-cured resin

materials that are both photo- and auto-polymerized (amine-peroxide system). Despite their autonomous onset, two distinct ways of polymerization initiate free radical formation and monomer conversion, which normally crossover one another during polymerization process. Photoactivation ensures initial stability needed to combat clinical tensions, while chemical activation ensures the mechanical properties over time.[32] In dual-cure resin cement, the remnant unreacted monomers after photo-activation get polymerized further by chemical activation, and therefore, the UM content diminishes further with time with higher physicomechanical properties than the individual photo or chemical activation.[33,34] Likewise, in the present novel photon-thermal polymerized P(MMA-*co*-DMAEMA), the UM, after photopolymerization, would be polymerized eventually during thermal polymerization, thereby reducing the UM content in the copolymer. Hence, from the above context, the novel photon-thermal dual-polymerizable DBR formulation was developed in this research, which contains DBPO as peroxide initiator for thermal activation and CQ as a photoinitiator for photoactivation.

In this current research, concentrations of 5, 10, and 15% of the CQ-DMAEMA complex were substituted. The copolymerizing ability of DMAEMA with MMA and the DC more than 15% of the CQ-DMAEMA complex has not been experimented with yet. One of the prime disadvantages of CQ is the yellow discoloration over time. Hence, it is necessary to evaluate the color stability of the DBR at various time intervals. Nevertheless, the effect of this addition on the shelf life of the TP-DBR has also to be evaluated. This is the only research with the CQ-DMAEMA complex in TP-P(MMA) successfully executed in developing a novel dual-cure DBR by the photon-thermal dual polymerization, and therefore, the results ought to be deciphered carefully. Future experiments are sought by increasing the concentration of the CQ-DMAEMA complex and its effect on the mechanical properties and biocompatibility.

Conclusion

Adhering to the research protocol and within the constraints of the study, it is concluded that the addition of DMAEMA successfully copolymerized with TP-P(MMA) to form a novel photon-thermal dual polymerized denture base copolymer P(MMA-*co*-DMAEMA) exhibiting higher DC than the control P(MMA). The P(MMA-*co*-DMAEMA) with 15% CQ-DMAEMA complex possessed the highest DC.

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