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Original Article

Copolymerization of Ring-Opening Oxaspiro Comonomer with Denture Base Acrylic Resin by Free-Radical/Cationic Hybrid Polymerization

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ABSTRACT

Background: Polymerization shrinkage is an innate characteristic of thermo-polymerized denture base acrylic resin. Volumetric shrinkage is still a problem, although myriad material modifications. Ring-opening oxaspiro monomers have promising volumetric expansions of about 7%. These monomers have diminished the shrinkage in dental filling resins through copolymerization (CP). However, their CP with denture base resins is not reported yet. **Purpose:** The aim is to confirm the CP of an oxaspiro monomer with methyl methacrylate (MMA) by radical-cationic hybrid polymerization and to assess the degree of conversion (DC) of the formed copolymer. **Materials and Methods:** The oxaspiro monomer was synthesized by a transesterification reaction. The study groups were based on the composition and thermo-polymerization method. The control and E1 groups were thermo-polymerized in water-bath, whereas the E2 group in a laboratory autoclave. Both E1 and E2 groups contained the oxaspiro monomer and cationic initiator. E2 group had an additional radical initiator. The CP and DC were confirmed and assessed by infrared spectroscopy. **Results:** Accentuation of carbonyl peak, the disappearance of the spiro-carbon peak, and the appearance of ether linkages in experimental groups confirmed the ring-opening. E2 group had the highest DC. **Conclusion:** The oxaspiro monomer successfully copolymerized with MMA and had good DC.

KEYWORDS: *Copolymerization, hybrid polymerization, oxaspiro monomer, polymerization shrinkage, spiroorthocarbonates*

INTRODUCTION

Poly(methyl methacrylate) (P(MMA)) resins are the most commonly used material for fabricating denture bases. Dimensional errors can occur from the step of denture wax-up to denture delivery to a patient.[1] Woelfel and Paffenbarge sketched out the errors inherent to the P(MMA) denture base material.[2] Dimensional changes during processing are one such source of error and are usually known as the processing errors. The processing shrinkage of thermo-polymerized P(MMA) is well documented in the literature.[3] To reduce the polymerization shrinkage, various polymerization methods and processing techniques were modified.[4] Concerning the material itself, numerous polymeric modifiers have been incorporated to dampen the shrinkage.[5] Several monomeric modifications have been executed with various comonomers in the literature.[6] A copolymer of P(MMA) from norbonyl-and phenyl-methacrylate comonomers showed decreased polymerization shrinkage.[7]

The advent of ring-opening monomers upon polymerization has a promising effect on the dimensional accuracy of a polymer by rendering it shrink-free.[8] Numerous ring-opening monomers emerged recently, possessing volumetric expansion

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upon polymerization. Spiro-ortho carbonates (SOCs) are one such ring-opening expanding monomer being widely researched and evaluated. Dimethylene tetraoxaspiro undecane (DMTOSU), a six-membered oxaspiro double ring-opening SOC monomer with two symmetrical exocyclic methylene groups, was used as a comonomer in dental composites to increase the adhesive fracture energy and to decrease polymerization shrinkage.[9,10] Nevertheless, the effect of adding DMTOSU as a comonomer in denture base resin has not been reported yet in the dental literature. A positive correlation concerning denture base resin's properties is expected with the formation of new copolymers with the addition of novel comonomers. Hence, establishing copolymerization (CP) of DMTOSU with P(MMA) becomes the primary concern in determining the material's physico-mechanical properties.

The advent of free radical-cationic hybrid polymerization (Rȯ-H^+) led to the development of hybrid polymers exhibiting excellent physico-mechanical properties as well as chemical resistance. Rȯ-H^+ offers additional control over polymerization kinetics, structure, and properties of the resultant polymer. Nevertheless, Rȯ-H^+ led to the development of numerous bizarre hybrid polymeric structures, including block, graft, random copolymers, and interpenetrating polymer networks.[11] DMTOSU monomer can polymerize by either free radical or cationic polymerization reaction. The polymerization cycle and technique determine the monomer to polymer conversion (degree of conversion [DC]). In denture base polymers, the DC is obtained from the ratio of aliphatic carbon-carbon (C═C) double bonds in a polymerized specimen to C═C bonds in an unpolymerized specimen. Therefore, the present study aims to confirm the CP of DMTOSU with methyl methacrylate (MMA) by Rȯ-H^+ hybrid polymerization. The study also aims to assess the DC of the formed copolymer.

Materials and Methods

2-methylene-1,3-propanediol (MPD; $C_4H_8O_2$: 97%), tetraethyl orthocarbonate (TEOC; $C_9H_{20}O_4$: 97%), 1,3-dichloro-1,1,3,3-tetrabutyl distannoxane (DCBS; $C_{16}H_{36}Sn_2O$: 98%), P(MMA) polymeric powder (molecular weight: 350 × 10^3 g/mol), methyl methacrylate (MMA, containing ≤ 30 ppm mequinol as inhibitor, 99%), dibenzoyl peroxide (DBPO; $[C_6H_5CO]_2O_2$: ≥98%), di-*tert*-butyl peroxide (DTBP; $C_8H_{18}O_2$: 98%), boron trifluoride diethyl etherate [BFDE; $BF_3O(C_2H_5)_2$], and tricyclodecane dimethanol diacrylate (TCDDMDA; $C_{18}H_{24}O_4$: cross-linker) were purchased from Aldrich Co.(Sigma-Aldrich, St. Louis, MO, USA) and used without further purification.

In a three-necked flask provided with a magnetic stirrer, condenser, nitrogen inlet, and thermometer, were put in 2 g of molecular sieves and 60 mL of toluene. MPD and DCBS were added and stirred for 15 min. This was followed by the addition of TEOC and Na_2CO_3. The mixture apparatus was flushed with nitrogen to establish anhydrous conditions. After the transesterification time, the reaction mixture was filtered and the solvent was rotoevaporated, obtaining DMTOSU as a white solid that was recrystallized from *n*-hexane. Infra-red (IR) spectrum (potassium bromide): Double bond C=C (1880, 1660, 1582 cm^{-1}), tetraoxaspiro linkage O–C–O (1212 cm^{-1}), cyclic ether stretch C–O–CH_2 (1095 cm^{-1}); Proton nuclear magnetic resonance (^{1}H-NMR) δ 4.5 (singlet, 8H,–OCH_2–), δ 4.95 (doublet, 4H, =CH_2); Carbon NMR (^{13}C-NMR) δ 117.12 (central spiro-C), δ 109.87 (=CH_2). To increase the dissolution rate of the crystals comparable to the polymerization rate, the crystalline DMTOSU was dissolved in benzene and injected into liquid nitrogen. The tiny droplets of the benzene containing the DMTOSU instantaneously froze and micro-fine crystalline DMTOSU precipitated. The liquid nitrogen was evaporated; the benzene was completely removed by freeze-drying in a desiccator and the resultant microcrystalline DMTOSU was vacuum stored at 5°C.[10]

The study groups were based on the composition and thermo-polymerization method. The powder/liquid ratio was 3:1. The control group (Con; n = 10) has P(MMA) powder with 2% DBPO and MMA with10% TCDDMDA. The dough forming time was 15 min and packed into 5 × 5 × 2 mm^3 mold space in dental stone in a brass flask and pressed at 3500 psi in mechanical press (Sirio Dental Srl, Meldola FC, Italy). After a post pressing time of 6 h, it was cured by short cycle in an acrylizer (Unident Instruments India Pvt. Ltd). The experimental groups E1 and E2 (n = 10 each) has P(MMA) powder with DBPO. In E1, MMA was incorporated with TCDDMDA and 4 mol% of BFDE. In E2 MMA, 4 mol% of DTBP was incorporated additionally. Since the microcrystalline DMTOSU was extremely moisture sensitive, it was immediately added at 20 wt% concentration into the powder-liquid mixture. The dough forming time was 20 min. The dough was packed and pressed for 6 h as above. For group E1, it was thermo-polymerized at 70°C for 2 h followed by the short-curing cycle in the acrylizer. For group E2, it was thermo-polymerized at 60°C for 45 min, followed by 130°C for 20 min in a digital vertical laboratory autoclave (Geeta industries, Jagadhri, Haryana, India). In all the groups, the flasks were allowed to cool to room temperature after curing, and then the specimens were retrieved.

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To confirm the CP and to assess the DC, Fourier Transform IR spectra in attenuated total reflection (ATR) mode (ThermoScientific™ Nicolet™ iS™ 5; iD1 Transmission, Waltham, MA; USA) was used. Concerning DC, the unpolymerized resin samples were prepared without adding initiators in all the groups. This eschewed the polymerization reactions between powder and monomer. To prepare the polymerized samples, the polymerized specimen's surface was trimmed with a tungsten bur. The uniform particle size of the resultant powder was obtained by sieving. The polymerized and unpolymerized samples were placed on the ATR crystal consecutively for the analysis. DC was determined from the ratio of the absorbance (Abs) intensities observed for aliphatic C═C (1640 cm^{-1}) to the carbonyl bond C═O (1720 cm^{-1}). The DC was calculated using the following equation:

$$DC\% = \left[1 - \frac{\left(\frac{Abs\,1640}{Abs\,1720}\right)_{Polymerized}}{\left(\frac{Abs\,1640}{Abs\,1720}\right)_{Unpolymerized}}\right] \times 100$$

The spectra of polymerized samples were used to confirm CP.

Statistical analysis was performed using the Statistical Package for the Social Science (SPSS) version 21.0 software version (SPSS Inc., Chicago, IL, USA). Preliminary results of the Kolmogorov–Smirnov test indicated the data of DC were normally distributed ($P > 0.05$). Descriptive statistics, including mean, standard deviation (SD), standard error, maximum, and minimum were calculated. Concerning inferential statistics, the level of significance between the groups for DC was tested with one-way ANOVA. To compare the groups, the *post hoc* Tukey's honestly significant difference (HSD) test ($\alpha = 0.05$) was performed. $P < 0.05$ was considered for statistical significance.

Results

The Fourier transform infrared spectroscopy (FTIR) spectra of the groups with highlighted differences (D1, D2, and D3 zones) are shown in Figure 1. Table 1 describes the functional groups and their corresponding wavenumbers of groups. The presence of aliphatic ether linkage peaks [(–C–O–CH_2–), (–CH_2–O–CH_2–)], accentuation of the carbonyl peak (C=O), and disappearance of tetraoxaspiro linkage peak in E1 and E2 groups confirmed the ring-opening of DMTOSU and its CP [P(MMA-*Co*-DMTOSU)]. Figure 2 depicts the ring-opening mechanism and cross-linking of the copolymer. Table 2 presents the mean and SD of the control and experimental groups. One-way

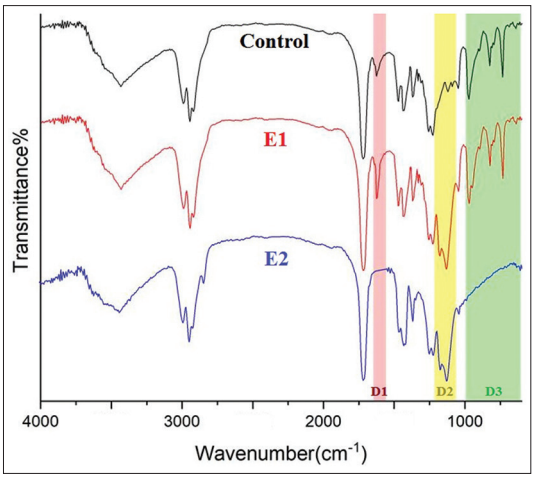

Figure 1: Fourier transform infrared spectroscopy-attenuated total reflection spectra of the groups

ANOVA showed significant differences among the groups ($P = 0.000$). Tukey's HSD multiple comparison tests [Table 3] showed a statistically significant difference between the groups ($P = 0.000$). The DC was high for the E2 copolymer and low for the E1copolymer. The control group had an intermediate DC.

Discussion

The formation of novel P(MMA-*Co*-DMTOSU) copolymer was evident from the FTIR spectra. In Figure 1, the peak at D1 zone (C=C) was accentuated for E1 than the control. This is ascribed to the pendant methylene group of the ring-opened poly(ether carbonate) (PEC) chain and residual MMA. However, the peak is absent in E2, which is suggestive of cross-linkage and little/no residual MMA. The presence of ether linkage peaks at the D2 zone in the experimental groups is suggestive of ring-opening and resulted in the PEC chain. The absence of peaks at the D3 zone in E2 is suggestive of cross-linkage, whereas, in E1, there is no evidence of the same. Nevertheless, the vinylidene bending peak of the control and E1 groups is suggestive of residual MMA. The control and E1 groups have *trans-and cis*-(C-H) wagging peaks. The *trans*-wagging peak is attributed to residual MMA of the control group. Both residual MMA and pendant methylene group of the PEC chain might be causing the *trans*-wagging in E1. *Cis*-wagging is purely due to the residual MMA. The trans-(C=C) bending and =CH_2 wagging in E1 are attributed to the pendant methylene group of the PEC chain. The accentuation of the carbonyl peak in the experimental groups is attributed to the C=O group resulted from ring-opening.

In the infrared charts of all groups [Figure 3], two Abs peaks were seen at 1640 cm^{-1} and 1720 cm^{-1} for unpolymerized samples that are ascribed to the unreacted

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Table 1: Fourier transform infra-red spectrum spectra of polymerized resins

Functional groups: Attributions	Wave numbers (/cm); peak intensity		
	Control group	Experimental groups	
		E1	E2
O–H stretch of physisorbed moisture	3436	3429	3418
CH_3 stretch (C–H)	2993	2970	2961
Aliphatic chain $–CH_2–$ stretch (C–H)	2951	2936	2934
Carbonyl stretch (C=O)	1731	1728	1728
Carbon-carbon stretch (C=C)	1637	1638	Absent
CH_2 asymmetric bending (C–H)	1481	1476	1473
CH_3 asymmetric bending (C–H)	1444	1439	1436
CH_3 α-methyl bend ($C–CH_3$)	1388	1372	1365
$C–O–CH_3$ stretch	1244	1240	1241
Aliphatic ether linkage I stretch ($–C–O–CH_2–$)	Absent	1202	1199
Aliphatic ether linkage II stretch ($–CH_2–O–CH_2–$)	Absent	1149	1147
Trans- (C–H) wagging	987	985	Absent
Trans- (C=C) bending	Absent	962	Absent
CH_2 wagging	Absent	905	Absent
Vinylidene (C=C) bending	888	885	Absent
Cis- (C–H) wagging	730	724	Absent

Table 2: Degree of conversion (%) - one-way ANOVA

Groups	Mean±SD	*F*	Significance
Control	92.09±0.57	555.408	0.000
E1	88.44±0.44		
E2	96.46±0.58		

SD: Standard deviation

Table 3: Degree of conversion (%) - *post hoc* Tukey's honestly significant difference test

Group (I)	Compared group (J)	Mean difference (I-J)	Significance
Control	E1	3.65100*	0.000
	E2	−4.36900*	0.000
E1	E2	−8.02000*	0.000

*The mean difference is significant at the 0.05 level

C═C of MMA. The Abs peak at 1640 cm^{-1} significantly disappeared with the polymerized samples of E2. This can be inferred as decreased or negligible residual MMA and cross-linking. However, for the polymerized samples of the control and E1 groups, Abs peak at ≈1640 cm^{-1} did appear, which suggests the presence of residual monomer. The Abs peak at ≈1650 cm^{-1} in E1 is attributed to the pendant methylene group of the PEC chain and therefore, E1 copolymer had the least DC.

P(MMA) denture base resins undergo Rȯ polymerization with DBPO as an initiator with a homolytic temperature >60°C. SOCs with *exo*-methylene groups can undergo both Rȯ and H^+ ring-opening polymerizations. The Rȯ polymerization is initiated by DTBP and *tert*-butyl hydroperoxide (TBHP). DBPO had little or no conversion.[12,13] Moreover, the homolytic temperature

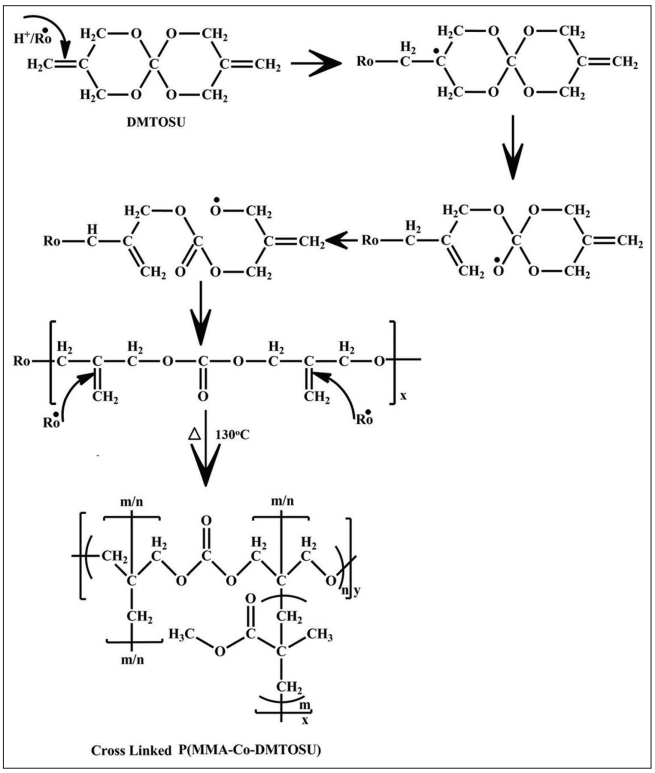

Figure 2: Ring-opening and copolymerization with cross-linking scheme

for TBHP is 172°C, which is impractical to use in denture base resins. The homolytic temperature of DTBP is >100°C. DTBP (3 mol%) at 120°C–130°C resulted in bulk polymerization that was cross-linked.[14] Hence, in the present study, DTBP was used in the E2 group. Regarding H^+ ring-opening polymerization of asymmetric SOC with BFDE initiator, the volume expansion was maximum (5.43%) at 55°C.[15] With symmetric DMTOSU

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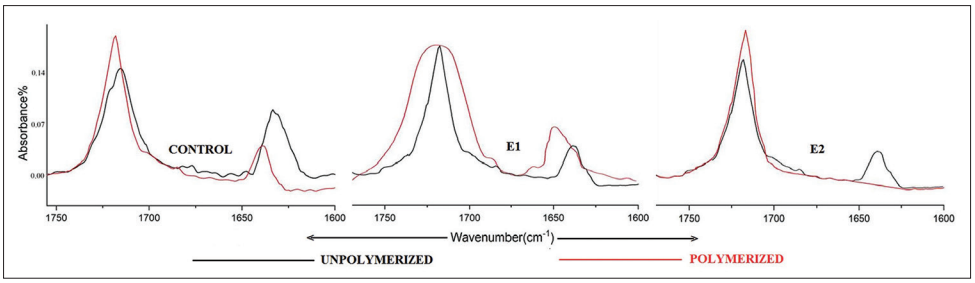

Figure 3: Fourier transform infrared spectroscopy spectra of unpolymerized and polymerized samples of the groups

homopolymerization with BFDE (1 mol%), 4.3% expansion was observed at room temperature and 7% expansion just below its melting point (82°C) at 70°C.[16] Therefore, the initial thermo-polymerizing temperatures were held at 70°C and 60°C for E1 and E2 groups, respectively anticipating volume expansion. Hence, in the present study, hybrid polymerization with Rȯ-H$^+$ (DBPO–DTBP–BFDE) initiator system was employed in the experimental groups.

Poly(monocyclic orthocarbonate) resulting from single ring-opening and non-ring-opening vinyl CP did not occur in the present study. The reason for this may be attributed to the hybrid polymerization initiator system. The homopolymerization of the liquid DMTOSU resulted in only a 2% expansion that necessitates a large amount of DMTOSU in a mixture to diminish the shrinkage. However, the crystalline DMTOSU exhibits a 4%–7% expansion based on polymerization temperature. Therefore, less quantity of crystalline material would be required to eschew shrinkage.[10] Hence, in the current study, micro-fine crystalline DMTOSU was used. Since the formation of P(MMA-*Co*-DMTOSU) copolymer was affirmed, further studies with increased concentrations and evaluating the mechanico-biological properties of the material are mandatory.

Conclusion

From the results, it is concluded that the DMTOSU double ring-opening oxaspiro monomer can be successfully used as a denture base comonomer. It readily copolymerized with MMA to form P(MMA-*Co*-DMTOSU) copolymer with increased DC.

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Nil.

Conflicts of interest

There are no conflicts of interest.

References

1. Garfunkel E. Evaluation of dimensional changes in complete dentures processed by injection-pressing and the pack-and-press technique. J Prosthet Dent 1983;50:757-61.
2. Woelfel JB, Paffenbarger GC. Dimensional changes occurring in artificial dentures. Int Dent J 1959;9:451-60.
3. Anderson GC, Schulte JK, Arnold TG. Dimensional stability of injection and conventional processing of denture base acrylic resin. J Prosthet Dent 1988;60:394-8.
4. Wong DM, Cheng LY, Chow TW, Clark RK. Effect of processing method on the dimensional accuracy and water sorption of acrylic resin dentures. J Prosthet Dent 1999;81:300-4.
5. Begum SS, Ajay R, Devaki V, Divya K, Balu K, Kumar PA. Impact strength and dimensional accuracy of heat-cure denture base resin reinforced with ZrO_2 nanoparticles: An *in vitro* study. J Pharm Bioallied Sci 2019;11:S365-70.
6. Ajay R, Suma K, Ali SA. Monomer modifications of denture base acrylic resin: A systematic review and meta-analysis. J Pharm Bioallied Sci 2019;11:S112-S125.
7. Umemoto K, Kurata S. Basic study of a new denture base resin applying hydrophobic methacrylate monomer. Dent Mater J 1997;16:21-30.
8. Sakai S, Kiyohara Y, Itoh K, Ishii Y. Synthesis of cyclic thioncarbonates and spiroorthocarbonates from bis (tributyltin) alkylene glycolates and carbon disulfide. J Org Chem 1970;35:2347-50.
9. Fu J, Liu W, Hao Z, Wu X, Yin J, Panjiyar A, *et al.* Characterization of a low shrinkage dental composite containing bismethylene spiroorthocarbonate expanding monomer. Int J Mol Sci 2014;15:2400-12.
10. Thompson VP, Williams EF, Bailey WJ. Dental resins with reduced shrinkage during hardening. J Dent Res 1979;58:1522-32.
11. Ge X, Ye Q, Song L, Misra A, Spencer P. Visible-light initiated free-radical/cationic ring-opening hybrid photopolymerization of methacrylate/epoxy: Polymerization kinetics, crosslinking structure, and dynamic mechanical properties. Macromol Chem Phys 2015;216:856-72.
12. Sanda F, Takata T, Endo T. Synthesis and radical polymerization of spiroorthocarbonates bearing exo-methylene groups. Macromolecules 1993;26:737-43.
13. Sanda F, Takata T, Endo T. Radical polymerization of 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5.5]undecane. Study of the structure of the polymer and mechanism of polymerization. Macromolecules 1993;26:729-36.
14. Endo T, Bailey WJ. Synthesis and radical ring-opening polymerization of spiro o-carbonates. J Polym Sci Pol Chem 1975;13:2525-30.
15. Endo T, Bailey WJ. Synthesis of monomers expanding on polymerization. Synthesis and polymerization of 3-methylene-1,5,7,11-tetraoxaspiro[5.5]undecane. Die Macromolekulare Chemie 1975;176:2897-903.
16. Bailey WJ, Endo T. Synthesis of monomers that expand on polymerization. Synthesis and polymerization of 3,9-dimethylene-1,5,7,11-tetraoxaspiro[5.5]undecane. J Polym Sci Pol Chem 1976;14:1735-41.