ORIGINAL RESEARCH

Structure, Surface Topography, and Glass Transition Temperature of Dental Poly (Methyl Methacrylate) Resin Conjugated with 3,9-bisethenyl-2,4,8,10-tetraoxaspiro [5,5] Undecane as Cross-linker: An *In Vitro* Research

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Abstract

Aim and objectives: To characterize and analyze the structural presentation of a new denture base copolymer with a spiro-acetal cross-linker at 10 and 20 wt.% concentrations by nuclear magnetic resonance (NMR) and field emission scanning electron microscopy-energy-dispersive X-ray (FESEM-EDX) spectroscopies. Also, to evaluate the glass transition temperature (T_G) of the new copolymer.

Materials and methods: The investigational groups G10 and G20 were heat-cured with the new spiro-acetal cross-linker at the above-mentioned concentrations, respectively. The control group G0 was heat-cured without the new cross-linker. Nuclear magnetic resonance and EDX spectroscopies determined the copolymerization along with elemental composition. The surface characteristics were discerned by FESEM. Differential scanning calorimetry was employed to evaluate the T_G of the resultant copolymer. Appropriate statistical operations were performed to compare the mean T_G of the groups.

Results: The new copolymer's structure with the spiro-acetal cross-linker was configured with protons, carbons, aluminum, zirconium, yttrium, and silicon atoms. The T_G of the resultant copolymer was high when compared with the G0. The 20 wt.% spiro-acetal cross-linker in the copolymer exhibited the highest T_G.

Conclusion: The spiro-acetal cross-linking comonomer incorporated in the heat-cure denture polymer produced a new denture base copolymer with elevated T_G. The resultant configuration of the new copolymer was characterized, structurally presented, and confirmed.

Clinical significance: The new copolymer might exhibit augmented strength due to the copolymerized spiro-acetal cross-linker. Moreover, the smooth and regular surface of the copolymer would have minimum or negligible microbial adhesion due to the hydrophobicity of the spiro-acetal comonomer incorporated in the denture base composition.

Keywords: Copolymer, Cross-linker, Denture base, Glass transition temperature, Spiro-acetal.

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Introduction

Dental polymers have been widely used in dentistry over a long period. The characteristic modifications that could be done in the material composition of the polymeric material accredit to its extensive application in dentistry. Dental poly (methyl methacrylate) [P (MMA)] resin is one such polymeric material that could be subjected to characteristic modification by altering the material composition which may enhance its physicomechanical and biological properties.[1] Poly (methyl methacrylate) is an amorphous linear-chain polymer more vulnerable to water sorption with relatively low impact strength, elastic modulus, and rigidity.

Also, P (MMA) is imperfectly elastic and undergoes delayed elasticity after deformation due to intermolecular forces exerted while trimming/polishing or cleaning/storing the dentures in hot water. At the glass-rubbery transition phase, energy dissipation after trimming/polishing (delayed elasticity effects) is at the maximum level and there would be delayed recovery from these deformations. It is apparent when P (MMA) is exposed to glass transition temperature (T_G) for a short duration, it behaves as a flexible material with accelerated permanent deformation.[2] Above

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the T_G, P (MMA) exhibits hysteresis (isotropic expansion) or serious dimensional aberrations upon cooling.[3]

The T_G is of great importance concerning thermo-cured denture base P (MMA). It greatly influences or amplifies dimensional inaccuracies in the dentures along with different expansion-contraction rates of the resin, polymeric teeth, and the invested gypsum that results in warpage.[4,5] The bonding between the polymeric teeth to the denture base is also dependent on or influenced by the T_G.[6] The T_G is affected by the type and concentration of the plasticizing agent.[7] Nevertheless, T_G is also affected by the type and concentration of cross-linkers included in the composition.[8,9] Positional shifts of large polymeric chains occur at T_G[10] and such shifts are governed by the molecular structure, branching, and degree of cross-link density.[11] Therefore, the T_G denture base P (MMA) should be greater than the temperatures exposed during trimming/polishing or when used *in vivo* to eschew thermal distortion. With the development of several new denture base materials, a thorough knowledge of T_G is indispensable, conspicuously when enhancements in mechanical properties can often be attained by chemical modifications that may decrease T_G. Such modifications do not mandatorily contribute to a material's improvement and emphasize that mechanical strength properties seldom be considered separately.[2]

Numerous modifications have been experimented on the denture base resins' composition and the liquid monomer modifications with comonomers are not uncommon.[1] The incorporated comonomer ought to chemically react/interact with the proprietary methyl methacrylate (MMA) through copolymerization (CP) to yield a novel copolymer with palatable properties.[12] This interaction can be resolved by nuclear magnetic resonance (NMR) and energy-dispersive X-ray (EDX) spectroscopies. The surface topography of the copolymers can be analyzed by field emission scanning electron microscopy (FESEM).[13]

3,9-bisethenyl-2,4,8,10-tetraoxaspiro [5,5] undecane (BETU) is a bicyclic hydrophobic spiro-acetal organic molecule with a central spiro atom to which two alicyclic rings are linked. When appended to polymers, the spiro-acetal moiety of BETU has manifested satisfactory adhesive properties, with improved flexibility and tensile strength.[14] Besides a horde of compositional/chemical modifications executed to develop new denture base polymeric materials with superior properties, the search and research for an ideal material are still on. However, the effect of adding BETU in the denture base P (MMA) resin as a cross-linker on the copolymeric structure, surface appearance, and the T_G of the resultant copolymer has not been reported in the literature yet. Hence, the present research aims to analyze the structural configuration, topography, and T_G of the new denture base copolymer with BETU at 10 and 20% concentrations. The null hypothesis was that the BETU incorporation in the denture base P (MMA) does not affect on the T_G upon evident CP.

Source of support: Nil

Conflict of interest: None

Materials and Methods

The research was conducted at the Central Electrochemical Research Institute in Karaikudi. Poly (methyl methacrylate) prepolymer powder (Molecular weight ~ 350,000 gm/mol), dibenzoyl peroxide initiator, methyl methacrylate liquid, n-butyl methacrylate plasticizer, ethylene glycol dimethacrylate cross-linker, BETU, were bought from Sigma-Aldrich (Acme ProGen Biotech [India] Pvt. Ltd. Tamil Nadu) and used as received. Inorganic fillers videlicet aluminum trioxide, yttrium-stabilized zirconia, and coupler γ-methacryloyloxypropyl trimethoxysilane were also procured from the same source. The silanization of the fillers with the coupler was executed by the method described by Kundie et al.[15] In P (MMA)-initiator mixture (0.5 wt.% initiator), 5 wt.% silanized fillers (1:1) was added and mixed for 1 h at 25 ± 1°C to form the powder complex. In an Erlenmeyer flask with a magnetic stirrer, the liquid component was prepared by mixing 10 wt.% plasticizer and 10 wt.% cross-linker in MMA for 30 minutes at 25 ± 1°C.

The groups were divided according to the BETU's concentration and composition in the cured specimens (Table 1). The present *in vitro* research consists of three groups—a control group G0 [without BETU] and two investigational groups G10 and G20 with BETU comonomer at 10 and 20 wt.% concentration, respectively. The powder and liquid compositions were uniform for all the groups except for the BETU's incorporation. To the powder-liquid mixture, BETU was added at the stipulated concentrations. The resultant dough was packed in the mold space and thermo-polymerized at 74°C for 8 hours with a terminal boiling treatment for 30 minutes.

For ^{1}H- and C-NMR, the polymerized specimens (n = 1 per experiment, per group) were ground to a fine powder which was then dissolved in one milliliter of deuterated chloroform ($CDCl_3$) and subjected to analysis employing an NMR spectrometer (Ascend™ 500; Bruker, GmbH, Germany) with tetramethyl silane as internal reference.[13] A cuboidal polymerized (unfinished and unpolished) specimen (n = 1 per group; 5 × 5 × 3 mm^3) was analyzed on FESEM-EDX. FESEM scanned the specimens' surface to characterize the topography (Germany: Carl Zeiss Supra 55VP; 5000× magnification). The elemental compositional percentage in the specimens was determined by EDX spectroscopy (JEOL-JSM-IT 200; Tokyo, Japan). The T_G was evaluated by differential scanning calorimetry (DSC) (Netzsch, STA 449 F3 Jupiter®, Selb, Germany). Ten polymerized specimens (n = 10) per group were finely powdered. On the aluminum mount off the calorimetry, 20 mg powder from each group was heated under a nitrogen environment from 50°C to 200°C at a constant rate of 10°C/min. In this research, the T_G was deduced by adhering to the technique followed by Ajay et al.[13]

Table 1: Study groups and their composition in polymerized specimens

Group	*Powder*	*Liquid*	*BETU*
G0	94.5 wt.% P (MMA) pre polymerized powder, 0.5 wt.% DBPO, 5 wt.% Al_2O_3-YSZ (1:1).	MMA with ≤30 ppm mequinol as an inhibitor, 10% n-butyl methacrylate (n-BMA) as a plasticizer, and 10% ethylene glycol dimethacrylate (EGDMA) as a cross-linker.	Absent
G10			10 wt.%
G20			20 wt.%

For a 3:1 powder-liquid ratio, the BETU was added to the powder-liquid mixture finally

Statistics concerning the T_G were performed using Statistical Package for the Social Sciences software (SPSS Inc., Chicago, Illinois, USA; version 28.0). The obtained data when subjected to normality tests (Shapiro–Wilks and Kolmogorov–Smirnov) was found to be normally distributed ($p > 0.05$). Therefore, one-way ANOVA and a *post-hoc* Tukey HSD test were used to analyze differences among and between groups, respectively.

Results

^{1}H-NMR Spectroscopy

The peak signals designated for the spiro-acetal ring protons (=O=CH_2=: δ 3.198–3.395; =CH_2=O=: δ 3.416–4.576) and the proton attached to tertiary carbon of acetal moiety (=O=ĆH(ĆH)=O=: δ 4.641–4.818) are conspicuous in both G10 and G20 groups. These peaks confirm the presence of BETU in the obtained polymer. The signals at δ 1.950–1.999 corresponding to =CH_2=ĆH= in the investigational groups confirm the CP of BETU with the P (MMA) and yielded a new denture copolymer P(MMA-Co-BETU). These signals were absent in the control group. Nevertheless, the signals at δ 5.498, 6.038 (C(CH_3)=CH_2) in the control group prove the presence of unreacted MMA which are absent in the G10 and G20 groups. Furthermore, the absence of signal peaks between δ 5.101–5.385 (=CH=CH_2) and δ 5.582–5.830 (=CH=) confirms the absence of residual BETU in the P(MMA-Co-BETU) copolymers of both the G10 and G20 groups. Figure 1 shows the H-NMR spectra of all the groups with the structure and their differences numbered.[1]

^{13}C-NMR Spectroscopy

The peak signals designated for the central spiro-carbon (δ 32.37), the ring carbons (δ 70.12, 70.56), and the tertiary carbon of acetal moiety (=O=ĆH(ĆH)=O=: δ 101.3) are exclusively found in both the investigational groups and are suggestive of BETU incorporation in the obtained polymer. The signals at δ 22 corresponding to =ĆH=CH_2= and at δ 40 corresponding to α–CH in the investigational groups confirm the CP of BETU with the P (MMA) and resulted in the new denture copolymer P(MMA-Co-BETU) formation. These signals were absent in the control group. Nevertheless, the signals at δ 126.11 (>C=CH_2) in the control group prove the presence of residual unpolymerized MMA which is absent in the G10 and G20 groups. This signifies a near-total conversion in the investigational groups. Furthermore, the absence of signal peaks at δ 119.11 (=CH=CH_2) and δ 134.20 (=CH=CH_2) confirms the absence of residual BETU in the P(MMA-Co-BETU) copolymers of both the G10 and G20 groups. Table 2 tabulates the ^{1}H-NMR and C-NMR peak intensities (δ/ppm) of the groups.[13] Figure 2 shows the C-NMR spectra of all the groups with the structure and their differences numbered.[13]

FESEM-EDX

The surface of the control specimen showed an irregular and rough with a peculiar "lamelliform" appearance. On the contrary, the investigational groups made of P (MMA-Co-BETU) copolymer exhibited a smooth and regular surface. Therefore, incorporating BETU in the P (MMA) decreased the surface irregularities on the resultant copolymer. The elemental composition of the control and investigational groups was tabulated in Table 3. All the groups comprised carbon, oxygen, aluminum, zirconium, yttrium, and silicon atoms. Figure 3 depicts the FESEM-EDX spectra of the groups in the research.

Glass Transition Temperature (T_G)

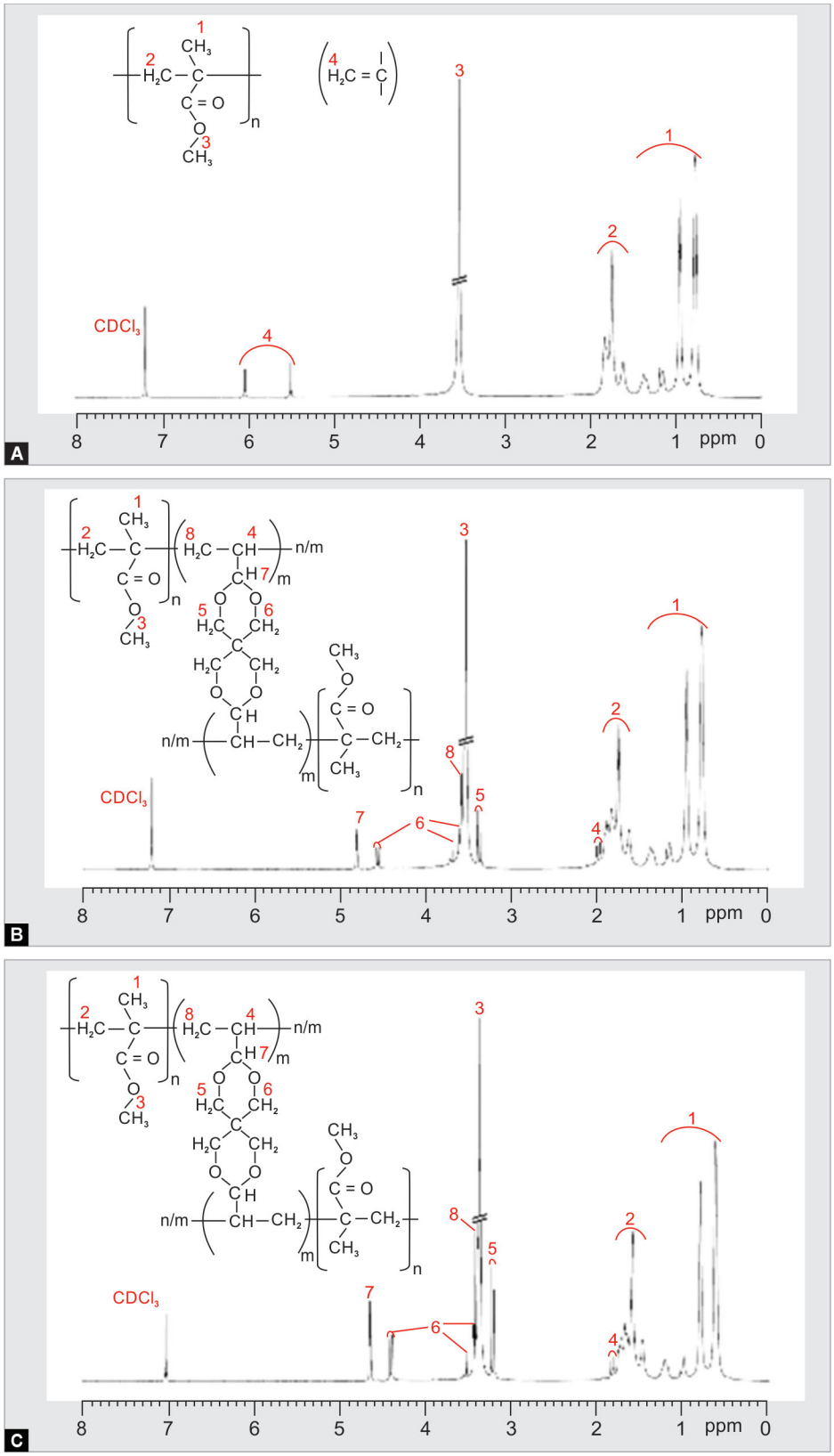
The mean T_G (°C) of the G0, G10, and G20 groups was 86.27, 101.28, and 121.21, respectively. A significant difference was there among and between the groups ($p = 0.000$) (Fig. 4). The P (MMA-Co-BETU) copolymer with 20% BETU had the highest T_G. Therefore, the addition of BETU in P (MMA) increased the T_G of the resultant copolymer.

Discussion

BETU's CP with MMA and the new copolymer P (MMA-Co-BETU) were affirmed by NMR and EDX spectroscopies. The T_G of the copolymer was also determined in the current research. The chemical structure of the P (MMA) was thrivingly transfigured by the incorporation of the spiro-acetal-based BETU comonomer resulting in the new P (MMA-Co-BETU) copolymer. The CP in the investigational groups was confirmed using NMR by detecting BETU's additional protons and carbons. Ajay et al.[13] copolymerized a cycloaliphatic cross-linker with the P (MMA) and NMR and EDX spectroscopies were employed for the CP confirmation. Substitution of this comonomer resulted in better physico-mechanical and biological properties of the resultant copolymer.[16,17] In another study, antimicrobial cross-linking acrylate monomer was copolymerized with P (MMA) and prosperously developed an antimicrobial denture base resin where the CP was studied by NMR spectroscopies.[18] A multifunctional acrylate cross-linking monomer was copolymerized with the dental composite resin and the formation of the copolymer was determined by FTIR and NMR spectroscopies.[19]

In the current research, the copolymer P (MMA-Co-BETU) exhibited higher T_G than the control group (PMMA). This coincides with the previous study where the addition of antimicrobial cross-linking comonomer in the P (MMA) increased the T_G in the trial groups. Also, Stutz et al. postulated that the cross-linking density and degree of cure are directly proportional to the T_G.[20] However, a credible relationship between the T_G and the cross-linking agent has not been determined yet. Divinyl cross-linking comonomer in P (MMA) appreciably modified the T_G as demonstrated by Jerolimov et al.[21] Nonetheless, the relation among T_G, cross-linkers chain length, and concentration is an obfuscating association. Myriad heat-curing cycles can cause anomalies in the T_G till 20°C.[22] Besides BETU, multitudinous cross-linking comonomers were experimented with denture base resins and assessed their influence over the T_G.[12] Conspicuously, long C-chained fluoro-monomers, cycloaliphatic acrylate cross-linker, and triazine triacrylate cross-linker increased the T_G of the P (MMA).[13,18,23,24] Conversely, itaconate comonomers and nitro-monomers lowered the T_G of the same.[25–27] Therefore, in that respect, it can discerned that the cross-linking comonomer's type strongly influences the T_G of the resultant copolymer.

Another confounding factor influencing the T_G is the cross-linking efficiency of the cross-linker, which is not always 100%. Residual monomers and partially polymerized pendant methacrylate moieties act as plasticizers that reduce the T_G. At high cross-linker concentrations, the efficiency of the polymerization reaction is low due to the high plasticizing potential of the unreacted pendant moieties.[21] In the present research's investigational groups, the NMR spectroscopies elicited meagre or negligible residual monomers (either MMA or BETU). Hence, there is hardly any chance for plasticization that caused the T_G hike in the P (MMA-Co-BETU). Moreover, the cross-linking efficiency and the cross-linkers chain



Figs 1A to C: ^{1}H-NMR spectra of the groups. (A) G0; (B) G10; (C) G20

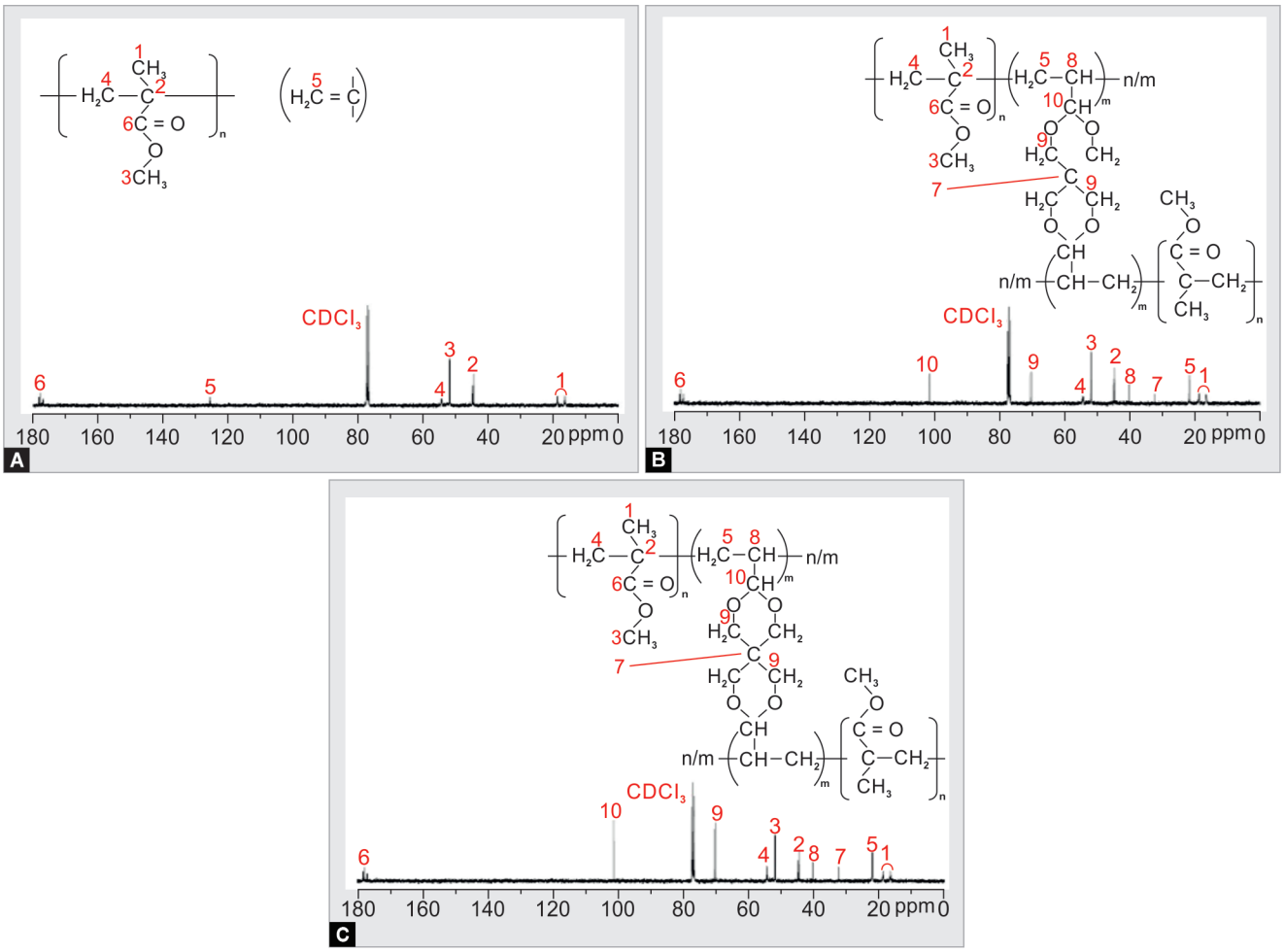
Table 2: ^{1}H-NMR and ^{13}C-NMR peak intensity (δ/ppm) values of the groups

	Group (δ/ppm)		
^{1}H-NMR: Protons of the ingredients	*G0*	*G10*	*G20*
┤C=CH_3	0.775–1.372	0.774–1.369	0.774–1.370
┤C=CH_2=C├	1.612–1.881	1.620–1.879	1.642–1.711
=CH_2=ĆH=	Absent	1.963–1.999	1.950–1.981
Spiroacetal =O=CH_2=	Absent	3.365, 3.395	3.198, 3.364
=O=CH_3	3.532	3.530	3.388
=CH_2=ĆH=	Absent	3.605	3.410
Spiroacetal =O=CH_2=	Absent	3.612–4.579	3.416–4.413
Acetal =O=ĆH(ĆH)=O=	Absent	4.807, 4.818	4.641, 4.652
C(CH_3)=CH_2	5.498, 6.038	Absent	Absent
=CH=CH_2	Absent	Absent (between 5.101 and 5.385)	
=CH=	Absent	Absent (between 5.582 and 5.830)	
^{13}C-NMR: Carbons of the ingredients			
α–CH_3	16.45, 18.68	16.48, 18.72	16.45, 18.72
=ĆH=CH_2=	Absent	22.13	22.16
Central spiro-carbon	Absent	32.37	32.37
α–CH (Tertiary carbon)	Absent	40.05	40.08
┼C (Quaternary carbon)	44.53, 44.89	44.53, 44.88	44.54, 44.89
┤C=CH_2=	54.43	54.44	54.40
=O=CH_3	51.86	51.85	51.85
=CH_2= attached to spiro-carbon	Absent	70.12, 70.56	70.12, 70.56
=O=ĆH(ĆH)=O=	Absent	101.33	101.32
=CH=CH_2	Absent	Absent (at 119.11)	Absent (at 119.11)
>C=CH_2	126.11	Absent	Absent
=CH=CH_2	Absent	Absent (at 134.20)	Absent (at 134.20)
C=O (Ester)	177.02, 177.84, 178.14	177.01, 177.83, 178.13	176.96, 177.83, 178.13

length are inversely proportional. Therefore, the T_G's dependency on the cross-link chain length may be elucidated by compromised cross-link efficiency and copolymerization.[21] In the current research, BETU lacks a long C-chain and instead has a double-ringed spiro-moiety which could be another reason for increased T_G in the new copolymer P (MMA-Co-BETU).

Long cure cycles of more than 7 hour at 70°C with a terminal boil are to be preferred. Such cycles produce polymers with low residual monomer levels and ensure optimized mechanical properties without compromising the dimensional accuracy of the polymers.[28] Jerolimov et al.[28] showed the curing cycle without the terminal boiling produced P (MMA) with the least T_G. The curing cycle with terminal boiling yielded polymers with the highest T_G. Nevertheless, the polymers with low residual monomers exhibit high T_G.[28] This is due to the reduced plasticizing effect of the residual monomer. Moreover, non-polymerizable plasticizers like phthalates in the P (MMA) decrease the T_G.[7] Therefore, in the present research, polymerizable plasticizer (n-BMA) and terminal boiling in the curing were employed which eventually contributed to the high T_G of P (MMA-Co-BETU). The heating rate of 10°C/min was opted for in the present research since it provided adequate probe sensitivity and avoided overheating of the specimens yielding elevated values of T_G.[28]

The tacticity of a polymer also influences the T_G. The T_Gs for some atactic P (MMA) powders were more than 105°C. Free-radical heat-curing at 60°C rendered the P (MMA) predominately syndiotactic with a T_G of 119°C.[29] The control P (MMA) in the current research manifested a T_G of 86.27°C (>119°C). This is owing to the n-BMA plasticizer in the polymer. However, with an increase in the curing temperature, the ensuant polymer turns highly atactic. In this research, a long curing cycle with terminal boiling was employed. Therefore, the formed copolymer P (MMA-Co-BETU) was atactic with amorphic microstructure and not crystalline. Any amorphous polymer exhibits a high entropy value owing to amplified disordering resulting in high T_G. Accordingly, this could be the plausible description for the high T_G for the P (MMA-Co-BETU) copolymer. An increase in the molecular weight decreases the chain end concentration and free volume consecutively raises the T_G in straight-chain polymers. In the present research, pre polymerized P (MMA) powder with a molecular weight of 350 × 10^3 gm/mol was employed in all the groups. On that account, the increased T_G of the investigational groups was solely accredited to



Figs 2A to C: ^{13}C-NMR spectra of the groups. (A) G0; (B) G10; (C) G20

Table 3: Elemental atomic composition of the groups in mass%

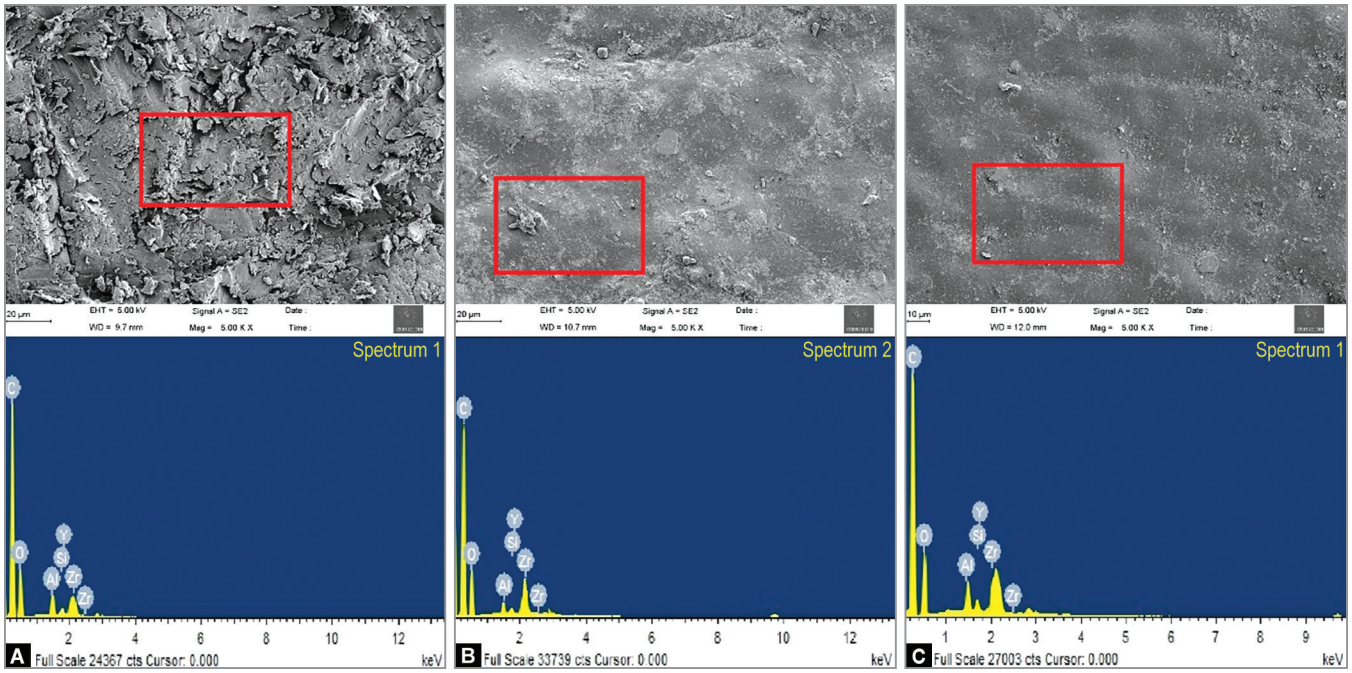
Group	*C*	*O*	*Al*	*Zr*	*Y*	*Si*
G0	65.15	31.52	1.51	1.46	0.19	0.17
G10	65.73	30.93	1.53	1.50	0.15	0.16
G20	66.17	30.46	1.52	1.51	0.17	0.17

the BETU cross-linking comonomer. Concerning polystyrene, the T_G and the molecular weight were directly proportional.[30] Other confounding factors like branching, polymeric chain length, the bond interactions, and rigidity of the polymeric chain governing the T_G are beyond the discussion's scope.

Only two concentrations of BETU were experimented with the denture base resin. The copolymerizing capacity of BETU with P (MMA) and its consecutive effect on the T_G more than 20% is yet to be tested. This experimental research is the only study to employ a spiro-acetal comonomer in the denture resin. Therefore, the results and inferences from this research should be deciphered with discretion. Future research should be performed concerning other vital physico-mechanical properties and biocompatibility by raising the BETU's concentration.

Conclusion

Within the research's limitations, the resultant configuration of the new P (MMA-Co-BETU) copolymer was characterized, structurally presented, and confirmed. The BETU spiro-acetal cross-linking comonomer successfully copolymerized with the denture base P (MMA) with regular surface topography. The P (MMA-Co-BETU) copolymer also possessed a high TG when compared to the denture polymer without the BETU cross-linker.



Figs 3A to C: FESEM-EDX spectra of the groups. (A) G0; (B) G10; (C) G20

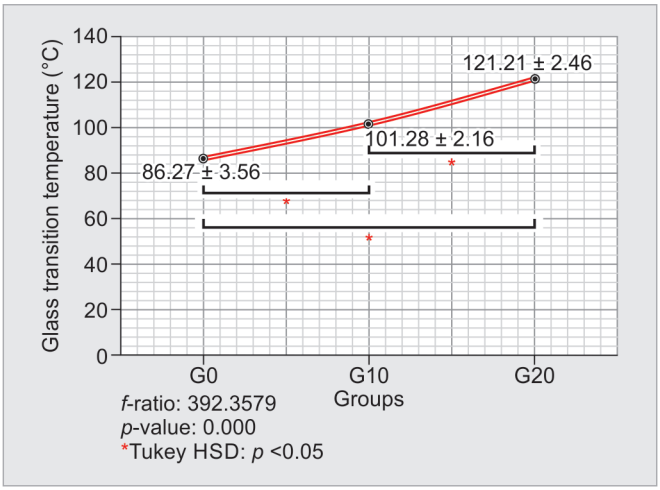


Fig. 4: Comparison of the T_G among and between the groups

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