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Flexural strength of polymethyl methacrylate copolymers as a denture base resin

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To improve the flexural strength and flexural modulus of polymethyl methacrylate (PMMA), copolymerization of PMMA with 10, 20, 30, and 40% (v/v) of either ethyl-methacrylate, butyl-methacrylate (BMA), or isobutyl-methacrylate (IBMA) was carried out. Test specimens were fabricated from heat-cured resin. The flexural strength was measured using a 3-point bending test. The chemical characterization and the copolymerization mechanisms of the copolymer resins were confirmed by ^{1}H-NMR and FTIR. The flexural strength data were analyzed by applying two-way variance analysis. PMMA was reinforced by ethyl-methacrylate, BMA and IBMA copolymerization. Flexural strengths of the BMA and IBMA copolymers were significantly higher than those of the control group. Maximum flexural strength and modulus resulted from a 40% concentration of IBMA. The flexural strength and modulus values of all copolymer groups were found to be higher than those of the control group. The flexural moduli of the BMA and ethyl-methacrylate groups were similar to those of the control.

Keywords: Copolymer, Denture bases, Mechanical property

INTRODUCTION

Denture base materials are composed of an acrylic resin mostly made up of polymethyl methacrylate (PMMA)[1,2]. The major shortcomings that limit the use of PMMA are its inadequate flexure strength properties[1]. Flexural fatigue of the prosthetic material usually results from chewing forces including compressive, tensile and shear stresses[2].

This shortcoming can be overcome with the addition of fracture-resistant materials to the PMMA resin. In that regard, alterations of the mechanical properties of PMMA by chemical modification or by adding material into the resin have been attempted[1,3-5]. However, a satisfactory alternative material to PMMA has not yet been developed[3,4,6,7].

The primary method of chemical modification of a polymer is to convert it into a copolymer[8]. Copolymers have been used to strengthen the denture base[3]. A new material with better mechanical and chemical properties could be through by treatment of different monomers with each other in various volumetric proportions[9]. In this way, the flexural strength, flexural modulus, impact strength, thermal durability, and adhesion properties may be improved[10]. It is known that the more cross-linking there is between the polymer beads, the higher the physical and chemical properties of resins, so the resin could exhibit superior properties to linear polymers[11]. Therefore, compared to linear polymers, copolymers exhibit greater polymerization rates, increased mechanical properties and lower water absorption properties[11].

Fluoroalkyl methacrylate, butadiene styrene, 2-hydroxyethyl methacrylate, isobutyl methacrylate, 1,3-bis(methacryloxypropyl) tetramethyldisiloxane, narbonyl, and phenyl methacrylate monomers were treated with methyl methacrylate to enhance the mechanical and physical properties of the denture base[3,6,7,12,13]. Although the results of previous studies differed from each other, an entirely alternative copolymer denture base resin to PMMA with entirely superior chemical and physical features was not found. Therefore, we hypothesized that the copolymerization of either ethyl-methacrylate (EMA), butyl-methacrylate (BMA), or isobutyl-methacrylate (IBMA) with PMMA would provide a copolymer which could be confirmed with FTIR and ^{1}H-NMR, and the end products would have better flexural strength and flexural modulus. The purpose of this study was to determine the mechanical properties, such as the flexural strength and flexural modulus, of copolymers obtained by treatment of PMMA with EMA, BMA, and IBMA, respectively.

MATERIALS AND METHODS

Specimen preparation

The specimens were fabricated from the PMMA based heat cured resin (QC-20, Dentsply, Addlestone, UK). For copolymerization three different methacrylate monomers —EMA (Sigma-Aldrich, Dorset, UK), BMA (Sigma-Aldrich) and IBMA (Sigma-Aldrich) were added to the monomer of PMMA which was the control group. All monomers were used in liquid form and all mixing ratios for the copolymer production were volumetrically determined. The chemical formula and the molecular weight of the monomers used in this study and the codes

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are given in Table 1. Specimens divided into 13 groups for all tests including flexural strength and flexural modulus (n=10, Table 2). The tests were carried out according to the protocol reported for flexural strength and flexural modulus by ISO standards[14,15]. The specimens in sizes of 64×10×3.3 mm were prepared for tests[14]. Specimens of the copolymer groups formed by the addition of volumetric percent of 10-20-30-40 of EMA, BMA and IBMA monomers to the monomer methyl methacrylate (MMA) of heat-cured resin. The polymer-monomer ratio was 23 g/10 mL in all groups. Polymerization has been carried out in accordance with the manufacturer's instructions. Then all specimens were polished with 600 grit sandpaper.

Flexural strength test

The specimens were stored in distilled water at a temperature of 37±1°C for 50±2 h before flexural testing. All the specimens from each group were subjected to flexural strength test under 3-point loading using a universal system testing machine (Lloyd LRX, Lloyd Instruments, Hampshire, UK). The distance between the supporting wedges was 50 mm and the cross-head speed used was 0.5 cm/min and engage the center of the specimen until the specimen fractured. Flexural strength and flexural modulus were automatically calculated.

^{1}H-NMR spectroscopy

An NMR spectrometer (Bruker DRX 400, Bruker BioSpin, Karlsruhe, Germany) was used for the ^{1}H-NMR spectra of all copolymer groups including the control group. A 5-mg resin sample was dissolved in 1 mL of deuterated chloroform ($CDCL_3$) (Sigma-Aldrich) and tetramethylsilane was preferred as an internal standard for the ^{1}H-NMR study.

FTIR analysis

Control and the copolymer resin groups were characterized by FTIR spectroscopy (FT/IR-430, JASCO, Tokyo, Japan). Polymerized specimens were dried using a dry-heat oven for 12 h at 70°C to eliminate H_2 molecules from the system. The specimens were cut into small pieces. One milligram sample size was used for each test group to acquire a clear FTIR spectrum.

Table 1 Chemical formula and molecular weight of the monomers used in this study and the codes

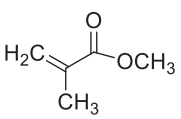
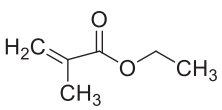
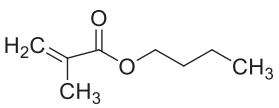
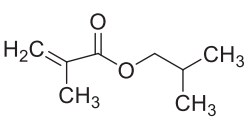
Monomer code	Molecular weight (g/mol)	Chemical formula
MMA	100.12	
EMA	114.14	
BMA	142.20	
IBMA	142.20	

Table 2 Volumetric percents of monomers

	100% MMA (Control)	
10% EMA+90% MMA	10% BMA+90% MMA	10% IBMA+90% MMA
20% EMA+80% MMA	20% BMA+80% MMA	20% IBMA+80% MMA
30% EMA+70% MMA	30% BMA+70% MMA	30% IBMA+70% MMA
40% EMA+60% MMA	40% BMA+60% MMA	40% IBMA+60% MMA

Statistical analysis

The data of flexural strength and modulus analyzed by applying two-way and cytotoxicity data were analyzed by applying the three-way analysis of variance. Bonferroni correction used for multiple comparisons.

RESULTS

The structure of the copolymerized compound was elucidated by spectroscopic techniques such as ^{1}H-NMR and FTIR. In FTIR spectrum, a robust stretching vibration signal of –C=O was observed at 1,730 cm^{-1}. C-O stretching band of esters appeared between 1,268 and 1,062 cm^{-1}. The stretching band of methyl and methylene –C-H appeared at 2,952 cm^{-1}, on the other hand, a – C-H bending signal of the same group appeared at 1,455 cm^{-1} (Fig. 1).

In the ^{1}H-NMR spectrum of poly(methyl methacrylate-co-ethyl methacrylate), methyls protons appeared at δ 0.86 and 1.05 as a singlet. The methylene protons were observed at δ 1.62 as a singlet. The methoxy group resonated at 3.62 as a singlet. The signal of the methylene protons of ester group appeared at downfield as a multiplet (δ 4.14) due to the electron delocalization effect of lone-pair electrons on oxygen atoms (Fig. 2). In the ^{1}H-NMR spectrum of poly(methyl methacrylate-co-butyl methacrylate), the methyls protons appeared at δ 0.87 and δ 1.05 as a singlet. The signal observed at δ 1.62

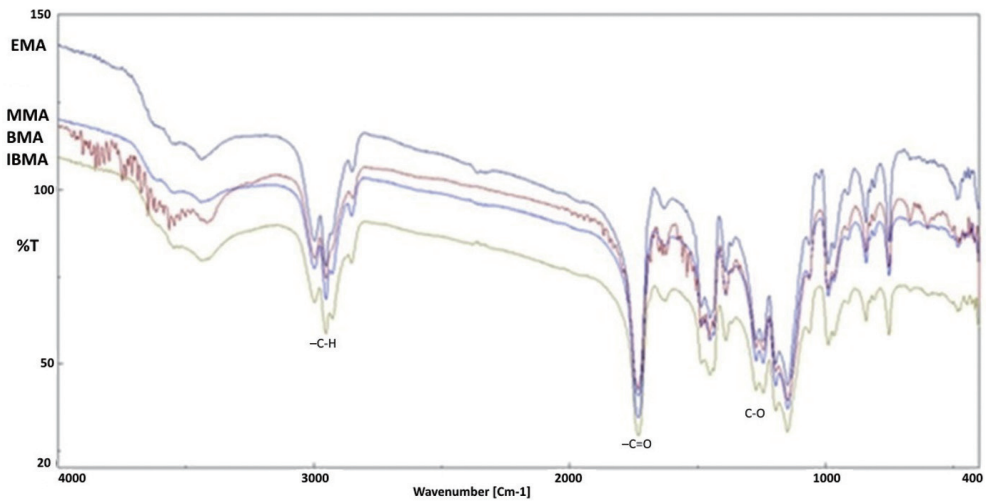


Fig. 1 FTIR spectrum of the monomers.

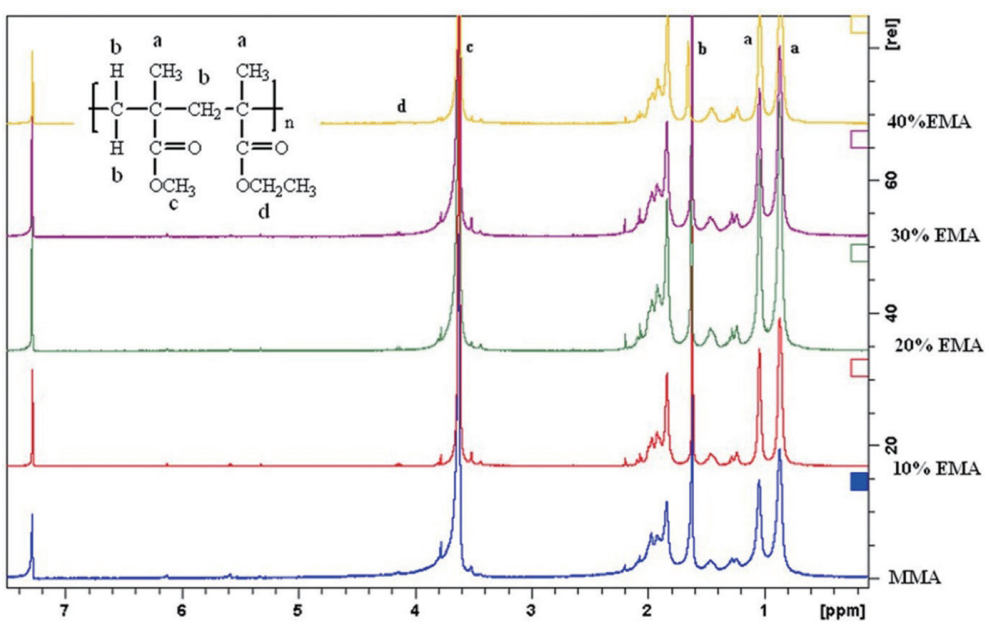


Fig. 2 ^{1}H-NMR spectrum of poly(methyl methacrylate-co-ethylmethacrylate).

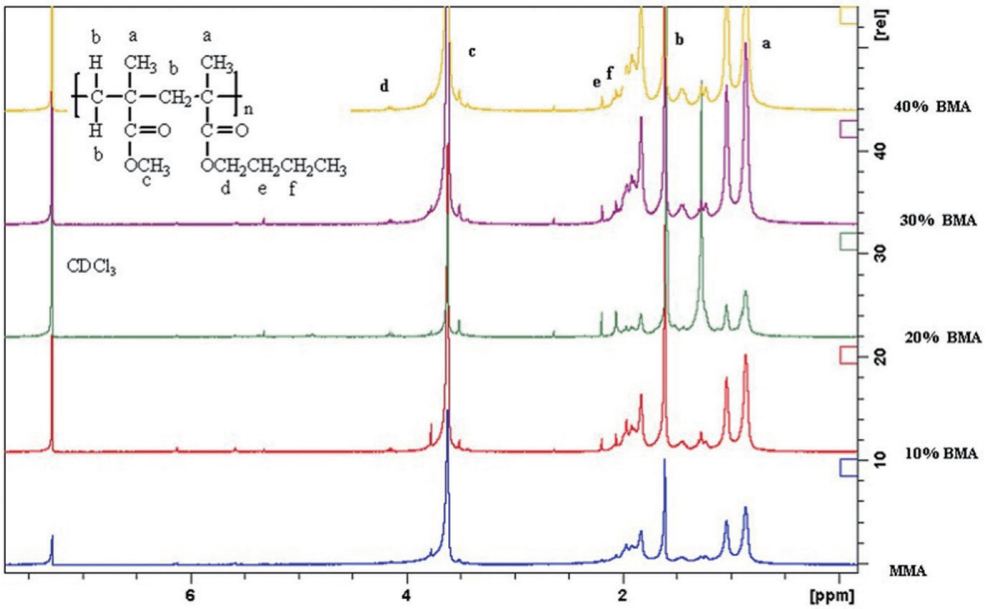


Fig. 3 ^{1}H-NMR spectrum of poly(methylmetacrylate-co-butylmetacrylate).

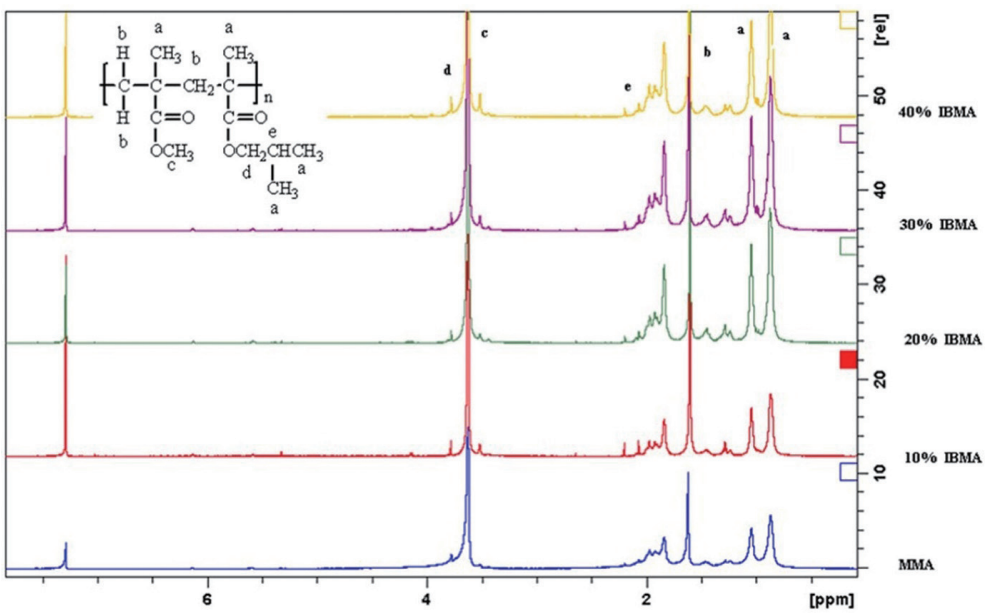


Fig. 4 ^{1}H-NMR spectrum of poly(methylmetacrylate-co-isobutylmethacrylate).

as a singlet belonged to the methylene protons. The ester group methylenes were observed at δ 2.07 and δ 2.20 as a multiplet. The signals observed at δ 3.63 consistent with the methoxy protons. The methylene protons bonding to the oxygen resonated at 4.15 as a multiplet (Fig. 3). In the ^{1}H-NMR spectrum of poly(methyl methacrylate-co-isobutyl methacrylate), the methyls protons appeared at δ 0.87 and δ 1.05 as a singlet. The signal observed at δ 1.61 as a singlet belonged to the methylene protons. The ester group of methylene proton was observed at δ 2.20 as a multiplet. The signals observed at δ 3.63 consistent with the methoxy protons. The downfield signal observed at δ 4.15 as a multiplet suit with the methylene bonding to the oxygen. Therefore, the spectral values accord with the structure (Fig. 4).

Regardless of the concentration rates, total BMA and IBMA copolymers were statistically different from the control group concerning flexural strength (p<0.05). While the flexural strength of the control group was 82 MPa, the flexural strength of the total EMA, BMA and IBMA copolymer groups was 86, 96 and 95 MPa, respectively. There was no statistically significant

Table 3 Flexural strength distribution by material and monomer concentration

Material	Concentration (%)	*n*	Flexural strength (Mpa) mean±SD
Control	Control	10	82.245±9.2(A)
EMA	10	10	82.114±16.642(x)
	20	10	90.963±14.786(x)
	30	10	78.783±8.06(x)
	40	10	91.891±11.217(x)
	Total	40	85.938±13.814(A)
BMA	10	10	95.773±7.705(x)
	20	10	95.688±9.769(x)
	30	10	91.126±6.458(x)
	40	10	101.673±12.427(x)
	Total	40	96.065±9.765(B)
IBMA	10	10	87.682±15.333(x)
	20	10	92.681±15.688(x)
	30	10	89.717±15.996(x)
	40	10	109.699±13.704(y)
	Total	40	94.945±17.062(B)
Total	Control	10	82.245±9.2(a)
	10	30	88.523±14.487(a)
	20	30	93.111±13.334(ab)
	30	30	86.542±12(a)
	40	30	101.088±14.146(b)
	Total	130	91.541±14.381

Two-way analysis of variance was used. (ABC): Intergroup difference for material (abc): Intergroup difference for concentration; (xy): Material x difference between groups for concentration. Bonferroni correction was used for multiple comparison. Significance level is 0.05.

Table 4 Two way ANOVA results of flexural strength test

Dependent variable: Flexural strength				
Source	Type III sum of squares	Mean square	F	*p*
Concentration (%)	2,819.165	939.722	6.535	<0.001
Material	5,508.234	1,836.078	12.769	<0.001
Concentration (%) *material	2,035.418	226.158	1.573	0.129

R-squared=0.634 (adjusted R-squared=0.564)

difference between the control group and total BMA and EMA copolymers concerning flexural modulus ($p>0.05$). Values of the flexural modulus of control and total EMA, BMA and IBMA groups were 2,430, 2,619, 2,839 and 2,933 MPa, respectively. When each group was evaluated in itself, it was observed that the concentration increase did not cause a statistical difference in the flexural strength and flexural modulus values except for 40% IBMA copolymer group ($p<0.05$). However, the flexural strength and the flexural modulus tended to increase numerically with increasing of concentration and the flexural strength and flexural modulus values of almost all copolymer groups were determined to be higher than the control group. The flexural strength and the modulus of the EMA groups was (82–92 MPa, 2,373–2,865 MPa), the flexural strength of the BMA groups was (96–102 MPa, 2,642–3,095 MPa), and the flexural strength and modulus of the IBMA groups was (88–110 MPa, 2,650–3,581MPa), respectively. Maximum flexural strength and modulus had been seen in the 40% IBMA (101 MPa, 3,580 MPa) copolymer group. Minimum flexural strength had been seen for the control groups (86 MPa, 2,430 Mpa) and the 30% EMA groups showed the lowest flexural modulus (2,373 MPa). Means and standard error of means of flexural strength and flexural modulus are shown in Tables 3–6.

Table 5 Flexural modulus distribution by material and monomer concentration

Material	Concentration (%)	*n*	Flexural modulus (Mpa) mean±SD
Control	Control	10	2,429.579±258.92(A)
EMA	10	10	2,463.266±355.548(x)
	20	10	2,776.331±417.666(x)
	30	10	2,372.683±437.596(x)
	40	10	2,864.518±460.244(x)
	Total	40	2,619.199±453.961(A)
BMA	10	10	2,826.982±385.172(x)
	20	10	2,642.029±377.012(x)
	30	10	2,792.661±210.699(x)
	40	10	3,094.883±431.881(x)
	Total	40	2,839.139±384.252(AB)
IBMA	10	10	2,650.391±476.889(x)
	20	10	2,768.308±472.077(x)
	30	10	2,733.554±671.218(x)
	40	10	3,580.721±600.348(y)
	Total	40	2,933.243±660.501(B)
Total	Control	10	2,429.579±258.92(a)
	10	30	2,646.88±422.692(a)
	20	30	2,728.889±413.915(a)
	30	30	2,632.966±498.668(a)
	40	30	3,180.04±572.423(b)
	Total	130	2,768.916±518.932

Two-way analysis of variance was used. (ABC): Intergroup difference for material (abc): Intergroup difference for concentration; (xy): Material x difference between groups for concentration. Bonferroni correction was used for multiple comparison. Significance level is 0.05.

Table 6 Two way ANOVA results of flexural modulus test

Dependent variable: Flexural modulus				
Source	Type III sum of squares	Mean square	F	*p*
Concentration (%)	4,518,048.878	1,506,016.293	8.746	<0.001
Material	6,132,264.905	2,044,088.302	11.871	<0.001
Concentration (%) *material	3,910,291.597	434,476.844	2.523	0.010

R-squared=0.570 (Adjusted R-squared=0.604)

DISCUSSION

The present study evaluated the mechanical effects of PMMA copolymers with either EMA, BMA, or IBMA. The results revealed that all copolymers, in agreement with the established hypothesis, provided improved flexural strength and flexural modulus.

The flexural strength of resin is an indicator of its hardness and resistance to fracture[13]. A flexural strength test is essential to determine the strength of the denture base against the masticatory forces. This test an indicator of tensile and compressive strength and elastic modulus[16]. In the present study, three different monomers having the same functional alkyl group were used to create a new copolymer with improved mechanical attributes.

Several studies are reported to have improved the mechanical properties of PMMA by chemical modification, such as by the addition of copolymer structures into the resin for the purpose of creating a rubber phase in the resin matrix. This resin was called a high-impact resin[5,9,17,18]. Rodford[5] was the first to present this method using low molecular weight butadiene-styrene rubbers (butadiene-styrene b-copolymer) to strengthen PMMA denture base polymers. Butadiene-styrene b-copolymers, which are macromers, were

polymerized. Then the macromer was dissolved in methyl methacrylate to obtain different copolymers. In this way, the PMMA/copolymer blend was formed. Rodford[19] studied the mechanical properties of this material and reported that high-impact denture base resins could be produced with macromer-methyl methacrylate copolymers. In the study, the butadiene-styrene b-copolymer played a role as a rubber phase in the blend. However, the flexural strength of conventional heat-cured acrylic resins has shown better results than that of high-impact resins[13,20]. At the same time, the incorporation of rubber has not been entirely successful in that it can contribute to reduced stiffness, enhanced creep, and water sorption[21,22]. The search for alternative materials for the denture base is still in progress. In the present study, a rubber phase was not used to obtain copolymer resins.

The addition of a monomer to a polymer is a matter of interest to obtain materials with superior properties that can be used as alternatives to PMMA[4,6,7]. Studies have reported that different monomers had been incorporated into MMA to reinforce PMMA[3,4,6,7,12,19,23-25]. Nonetheless, the results of these studies, though different from each other, failed to create a material superior to PMMA. Cunha *et al.*[3] examined the effect of fluoroalkyl methacrylate (10 and 20% [v/v], FMA) on the flexural strength of a denture base acrylic resin. The synthesized resin had a lower flexural strength and flexural modulus, possibly due to the different intermolecular distances caused by the presence of fluorine in the methacrylic polymers. Kurata *et al.*[4] studied three fluoro-substituted monomer and three styrene-type monomers; however, the resulting copolymer was also inferior to PMMA because of the presence of bulky and hydrophobic group monomers. The properties of the new material depend on the compatibility of the monomers forming the blend. However, if the polymer pairs do not react with each other, a material with inferior mechanical properties may be formed[9]. The Monomer groups that are compatible with each other have been shown to form copolymers with superior mechanical properties[26,27]. Therefore, monomers having the same functional group (methacrylate) as PMMA were preferred to form the copolymers in this study. In this way, it was intended to obtain copolymer formation without damaging the chemical resin matrix of PMMA.

A direct comparison of the mechanical properties of the PMMA copolymers with other copolymer studies could not be performed due to the differences in the copolymerization process, monomer type, and the ratio or mechanical test methods. According to ISO specifications[14]; flexural strength should not be less than 65 MPa and flexural modulus should not be less than 2,000 MPa for conventional heat-cured resins. All materials in the present study exhibited higher values of flexural strength and flexural modulus than the ISO guidelines. The flexural strength and flexural modulus of the control group were 82 and 2,430 MPa, respectively, and all test groups provided better values. The highest flexural strength was observed in the total BMA copolymer group (96 MPa). This was followed by the total IBMA group (95 MPa), the total EMA group (86 MPa), and the control group (82 MPa). The highest flexural modulus was observed in the total IBMA group (2,933 MPa). This was followed by the total BMA group (2,839 MPa), the total EMA group (2,619 MPa), and the control group (2,430 MPa). The flexural strength and flexural modulus tended to increase with increasing concentrations and the flexural strength and flexural modulus values of almost all copolymer groups were higher than those of the control group. The greater the concentration, the greater the changes in the maximum flexural strength and flexural modulus in the IBMA copolymer group. However, the BMA group had the lowest change in the flexural strength and modulus. The maximum flexural strength and flexural modulus were observed in the 40% IBMA group, while minimum flexural strength was observed in the 10% EMA group and the minimum flexural modulus was found in the control group. A possible cause of the changes in flexural strength and flexural modulus was the residual monomer content, which could plasticize the resin, reducing the interchain forces and resulting in deformation under loading[28]. Another factor that affected the physical properties was the polymerization degree of the copolymer, which is directly related to the molecular weight. Therefore, the polymerization degree through the molecular weight could affect mechanical strength[29]. Among the copolymers produced in the present study, EMA had the lowest molecular weight and the lower flexural strength observed in the EMA group might result from the lower molecular weight.

Copolymer type and the number of cross-linking agents in the polymer have significant effects on many properties of resins[30]. It is known that increased cross-linking between polymer beads improves the physical and chemical properties of resins and causes them to exhibit superior properties compared to linear polymers[11]. It was reported by Clark[31] that the binding of an alkyl group containing more carbons instead of the CH_3 group to the PMMA chain may increase the flexibility of the polymer. The addition of EMA, BMA, and IBMA, which contain higher numbers of carbon groups, into methyl methacrylate is thought to increase the flexural strength and flexural modulus of the copolymer groups. In other words, the copolymerization of PMMA with EMA, BMA, and IBMA could increase the flexural strength and flexural modulus values by the increasing the cross-linking in the polymer network.

Johnson and Jones[25] examined the effect of the copolymerization of PMMA with EMA and BMA on flexural modulus using concentrations of 25, 50, and 75% (v/v) EMA and BMA added to MMA. Contrary to our study, a decrease in flexural modulus was observed as the concentration ratio of the added monomer increased. In another study, Sahin *et al.*[12] used 2, 3, and 5% monomer ratios to perform the copolymerization of PMMA with IBMA. Their results showed that the flexural strength and flexural modulus of the 2% IBMA copolymer group was higher than the control group. However, the

flexural strength and flexural modulus of the IBMA groups showed a tendency to decrease with increasing concentrations, and the flexural strength and flexural modulus of the 3 and 5% IBMA groups were lower than those of the control group. Meanwhile, increasing the concentration did not cause any change in the flexural modulus values for the EMA and BMA groups in the present study. The reason why these results were not consistent with our study is thought to be due to the fact that the ratio of monomers used in the study was different from ours. More recently, Tugut *et al.*[32] reported that IBMA content in copolymers increased flexural strength; however, a decrease in flexural strength was found with an increase in monomer concentration. In the present study, an increase in monomer concentration provided an increase in flexural strength, which is contradictory to the Tugut *et al.*[32]A possible explanation could be the fiber content of the monomer used in their study.

The FTIR spectroscopic method is the most commonly used method for analyzing the structure of polymers[6,33]. Meanwhile, the chemical structures of denture base resins are usually evaluated by ^{1}H-NMR. In this study, the copolymerized acrylic resins were verified by both FTIR and ^{1}H-NMR spectroscopy. Methyl and methylene stretching of PMMA were observed in the FTIR spectra for all test groups. According to the FTIR spectroscopy results, the targeted polymer structures were obtained. In the FTIR spectra of both the control and copolymers, a strong –C=O (carbonyl) stretching band appeared at 1,730 cm^{-1}. Functional groups signaled at expected peaks. The carbon-carbon double bond peak of the methyl methacrylate monomer at 1,600 cm^{-1} disappeared, indicating the formation of the copolymer. In the ^{1}H-NMR spectra of MMA-co-EMA, MMA-co-BMA, and MMA-co-IBMA, methyl protons appeared at approximately 1 ppm as a singlet. The methoxy group resonated at 3.62 ppm as a singlet. In the ^{1}H-NMR spectrum, the expected methyl, methoxy group and methylene protons of the ester group resonated for each copolymer group. The ^{1}H-NMR spectral values accorded with the structure. These results confirmed that the copolymerization of PMMA with EMA, BMA, and IBMA was successful.

It might not be possible to transfer the present results directly to other studies because of the difference in the method, the monomer type, or the monomer ratio used in this study. The present study also has certain limitations. Firstly, only the flexural strength and flexural modulus were evaluated. Additional tests, such as impact strength, shear strength, water absorption, Vickers hardness, and surface roughness might be beneficial in determining the characteristics of the material. Secondly, residual monomer amounts should be determined. Finally, lower and/or higher concentrations should also be studied.

CONCLUSION

The present study synthesized three different copolymers of PMMA and evaluated their flexural strength and flexural modulus as mechanical properties. The copolymers were synthesized by treatment of EMA, BMA, and IBMA with MMA, and were verified by both FTIR and ^{1}H-NMR spectroscopy. The flexural strength and flexural modulus values of all copolymer groups were found to be higher than the control group, and a concentration-dependent increase was observed. In order to obtain better features than conventional heat cured resin, studies utilizing different volumetric percentages of the monomers and involving different mechanical and physical tests should be performed.

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