

Synthesis and Characterization of Acrylic-Based Photopolymer as a Candidate for Denture Base Material

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Abstract: Denture base is a denture part that rests on the soft tissue covering the jawbone and becomes an anchor of a denture. The material that commonly used for this purpose is poly (methyl methacrylate). However, it lacks in mechanical properties due to high water absorption. The aim of this research was to improve the physical and mechanical properties of poly (methyl methacrylate) by making a copolymer with styrene via photopolymerization process. In this method was used the addition of styrene monomer at 10, 20, 30, 40, and 50 wt% into the acrylic resin to form copolymer materials via photopolymerization process. The amount of 1.5 wt% Irgacure 784's photoinitiator was added as a photoinitiator. The results showed that the addition of 40% by weight of styrene copolymer is the best performance compare to the addition styrene of 10, 20, 30, and 50%. The samples with an addition styrene of 40 wt% showed excellent properties such as high water absorption value of $2.405 \mu\text{g}/\text{mm}^3$, the solubility of $0.434 \mu\text{g}/\text{mm}^3$, the flexural strength of 69.336 MPa, a flexural modulus of 1.236 GPa, and a hardness value of 82.583 HD. *Poly (methyl methacrylate-co-styrene)* copolymer with the addition of styrene 40 wt% has the closest value to the requirements for a denture base material.

Keywords: denture base, poly(methyl methacrylate-co-styrene), photopolymerization, Irgacure784.

1. Introduction

Many cases of tooth loss tend to increase along with the increasing growth rate of a country's population. It indicates that the use of dentures is growing. According to the Health Research conducted by the Ministry of Health of the Republic of Indonesia in 2007, the percentage of denture prostheses use in Indonesia reached 4.5% of the population, and 14.5% of the denture use was by the elderly over the age of 65 years [1]. The increasing use of denture prostheses also increased the demand for denture base [2].

Denture base is used as an anchor or base of the denture in soft tissue. Denture base must have biocompatible properties with the environmental bodies and have good mechanical properties so that it can withstand the forces due to the process of chewing and wear resistant to oral conditions [3]. In the fabrication of denture base, one type of polymer material that is frequently used is poly (methyl methacrylate), or PMMA. PMMA has excellent mechanical properties, but it has some drawbacks, such as poor water resistance and low mechanical strength due to water absorption [4].

Several attempts were made to improve the mechanical properties of PMMA, such as modifying the chemical structure and changing its polymerization techniques. The modification techniques commonly used a chemical structure of copolymer. In PMMA, the addition of copolymers does not only modify the physical properties of the conventional PMMA but also serves to improve toughness and impact resistance and prevent crack propagation [5]. Nearly 95% of denture base material uses



conventional polymerization method by heat or heat polymerization [6]. This approach has several disadvantages such as the requirement of energy (heat), low resistance to cracking, and the requirement of a complex mold design (mold). Photopolymerization Method is one novel method that has been used in dentistry to minimize those adverse effects resulted in such conventional polymerization methods [7]. When compared with the use of thermal polymerization, the polymerization process by using light has several advantages including small space requirement, less energy requirement, low temperature, waste-free (do not use solvent), and a simple work system [8]. The aim of this research was to improve the physical and mechanical properties of PMMA to form a copolymer of *poly (methyl methacrylate-co-styrene)* via photopolymerization process as the candidate material for denture base.

2. Experimental Method

The two processes were done in this study include the powder synthesis of poly (methyl methacrylate) as a powder component of acrylic resin and the copolymer synthesis of *poly (methyl methacrylate-co-styrene)* as a candidate material for denture base.

2.1 Synthesis of Poly-(methyl methacrylate) Powder

The synthesis process of poly (methyl methacrylate) powder was done for the purpose of producing the powder component in the acrylic resin and increasing the viscosity of the base material on the photopolymerization process. At this stage, methyl methacrylate monomer and heat-initiator benzoyl peroxide were used. The synthesis process began with the mix of methyl methacrylate monomer and 0.5% benzoyl peroxide by weight for 10 minutes at room temperature. Subsequently, the mixture was polymerized at a temperature of 85-90 °C for 1 hour. Then, the formed solid poly (methyl methacrylate) was crushed into fine powders. The poly (methyl methacrylate) was then characterized using the instrument of FTIR test and viscosity measurement (to determine the value of the resulted polymer molecular weight).

2.2 Synthesis of Poly-(methyl methacrylate-co-styrene)

The acrylic resins used was a mixture of the powder component and the liquid ratio with the comparison value of 1:3. The component of powder used was a powder poly (methyl methacrylate) which had been synthesized. Additionally, the liquid component consisted of a mixture of methyl methacrylate monomer and styrene with the addition of styrene varied to 10, 20, 30, 40, and 50 wt%. The acrylic resin that had been formed was then added an initiator of Irgacure 784, 1.5 wt%. Then the mixture was stirred for 10 seconds until it became homogeneous. The technique used was a fluid resin technique. The following photopolymerization process was carried out using the help of LED light curing units (LED-LCUs) via continuous curing methods (900 mW/cm² power density). This process was done gradually (layer by layer). The layering process was done by pouring the acrylic resins into the mold until it reached a thickness of 1-1.5 mm and then given up to a half polymerized blue light (half-cured). The allowed thickness of the acrylic resins was about 2-2.5 mm so that the light can get into the bottom layer. The light intensity should be recorded, while the LED LCUs located as close as possible to the surface of acrylic resin into the mold of ± 1 cm in order to harden the entire layer [9]. Furthermore, on the surface of the polymerized resin, the acrylic resin was poured back by using the same procedure. It was repeatedly done until the thickness of the polymer was synthesized to meet the allowed thickness of the mold. The white light exposure process was performed until the acrylic resin had been polymerized completely in the last layer. The copolymer of *poly (methyl methacrylate-co-styrene)* was then characterized using the instruments of FTIR, SEM, water absorption, flexural, and hardness test.

3. Results And Discussion

3.1 Characterization of Poly (methyl methacrylate) Powder

The comparison of infrared spectra of monomers methyl methacrylate (MMA) with poly (methyl methacrylate) (PMMA) FTIR test results is shown in Figure 1.

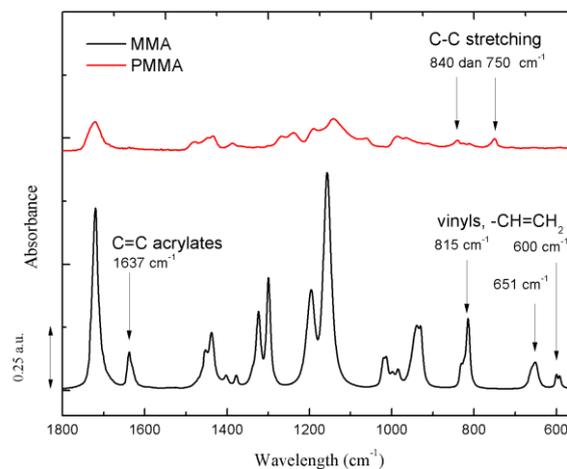


Figure 1. Infrared spectra of methyl methacrylate and poly (methyl methacrylate)

Based on the infrared spectra presented in Figure 1, there was a change in the absorption peak of methyl methacrylate in the forms of monomers and polymers. The shift was a shift in the intensity of the absorption in the wavelength of $\sim 1637\text{ cm}^{-1}$ (group C=C acrylates), ~ 600 , 651 , and 815 cm^{-1} (-CH=CH₂ vinyl group), and ~ 750 and 840 cm^{-1} (C-C stretching group) [10]. At the wavelength of $\sim 1637\text{ cm}^{-1}$, the intensity of the absorption decreased in the form of a polymer. In the form of monomers, there appeared the wavelength absorption peak at ~ 600 , 651 , and 815 cm^{-1} . In addition to the polymer, the wavelength of ~ 750 and 840 cm^{-1} appears on the wave absorption peak which did not appear in the infrared spectrum monomer. It indicated the termination of the C=C bond to -C-C- bond into the polymerization process. The severance of the bond indicated an addition to polymerization process performed to turn the methyl methacrylate into poly (methyl methacrylate) [11].

The results of the molecular weight calculation using the viscosity approach are given in Table 1.

Table 1. Molecular weight value of poly (methyl methacrylate) powder

Intrinsic Viscosity	Viscosity Parameter		Molecular weight (M _w)
	K (10 ⁻³ mL/g)	α	
36.76	7.7	0.70	180.115

The table showed the value of molecular weight poly (methyl methacrylate) powder, where K and α is a constant viscosity parameter of poly (methyl methacrylate) when dissolved in acetone using the method of viscosity [12]. The molecular weight poly (methyl methacrylate) which acted as the powder component in an acrylic resin might affect the mechanical properties of the denture base. The result of the molecular weight synthesized poly (methyl methacrylate) calculation in the research was 180.115 g/mol. It will tend to form long chain polymers with excellent physical and mechanical properties [13] with a molecular weight of above 100.000.

3.2. Characterization of Copolymer Poly (methyl methacrylate-co-styrene)

The infrared spectrum FTIR test results with a variety of additional styrene monomer in the copolymer poly (methyl methacrylate-co-styrene) were showed in Figure 2. In this figure, it appeared that the changes in FTIR spectra indicated the forming of a styrene functional group in the polymer chain. There were some changes to wave absorption intensity at a particular wavelength along with the addition of styrene [14] on the spectrum. Such changes occurred to the certain wavelengths of 700 and 780 cm^{-1} which indicate the group mono-substituted benzene in styrene, 1000-1300 cm^{-1} indicating the C-O group in the area of methyl methacrylate, 1600 cm^{-1} which indicating the C=C aromatic ring area of benzene in styrene, and at a wavelength of 1720 cm^{-1} indicating C=O groups on the carboxyl methyl methacrylate.

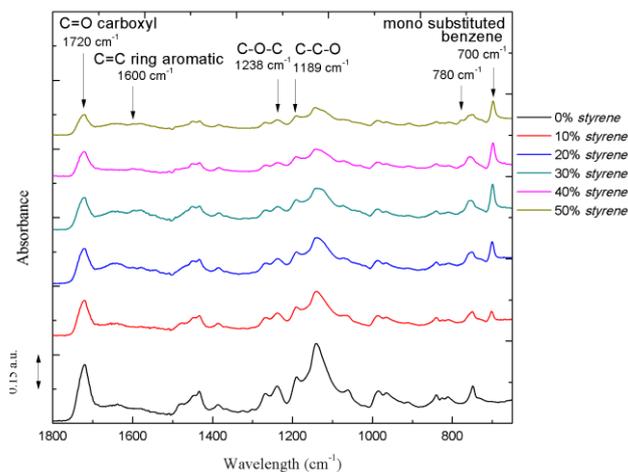


Figure 2. Infrared spectra of *poly (methyl methacrylate-co-styrene)* with a variation of styrene addition

Mono-substituted benzene group has two strong wavelengths of wave absorption, i.e. the wavelengths of 780 cm^{-1} and 700 cm^{-1} . Usually, only one wavelength alone raises the intensity of absorption in the spectrum [15]. Such fact indicated that the rate of absorption at the wavelength of 700 cm^{-1} was low and could only be identified by a high level monomer styrene addition (50%) to the copolymer, while the addition of low-level monomer styrene (10%) at the wavelength of 780 cm^{-1} to copolymers could already bring the peak in the spectrum of FTIR results. The presence of styrene which is included in the chain methyl methacrylate also caused dilation of peaks indicating C-O bond in methyl methacrylate groups [14]. It can be seen in the FTIR results presented in Figure 2 where the area from 1100 to 1300 cm^{-1} indicated the C-O bond dilation peak along with the addition of styrene. The peak was widening mainly at the wavelength of 1189 cm^{-1} , which indicated the C-C-O stretching peak, and at the wavelength of 1238 cm^{-1} , which indicated the C-O-C bending. The wavelength of $\sim 1600 \text{ cm}^{-1}$ indicated an area that showed the C=C stretching vibration in the aromatic ring appeared on styrene, while the wavelength of $\sim 1720 \text{ cm}^{-1}$ represented the area that indicated the carboxyl group C=O on the methyl methacrylate. The intensity of wave absorption at $\sim 1720 \text{ cm}^{-1}$ decreased along with the increasing addition of styrene concentrations. Along with the addition of styrene, there appeared a wavelength peak at $\sim 1600 \text{ cm}^{-1}$ indicating the benzene aromatic ring groups, but the value was small. The phenyl bond at 1600 cm^{-1} was weaker when compared with the carbonyl bond at 1720 cm^{-1} in the spectrum [14]. Figure 3 showed porosities that appeared in the cross-section copolymers with 1,000 times of magnification. The pictures show the porosity, which was indicated by a red circle, either on the polymer poly (methyl methacrylate) shown in Figure 3a or *poly (methyl methacrylate-co-styrene)* copolymer presented in Figure 3b until 3f. The addition of styrene monomer to 30 wt% (Figure 3d) caused the appearance of more cavity than other variations of additions. Then,

the addition of 50 wt% of styrene (Figure 3f) found that the cavity had a larger size than that in the addition of 40 wt% of styrene, and there were also small-sized cavities around the large cavity.

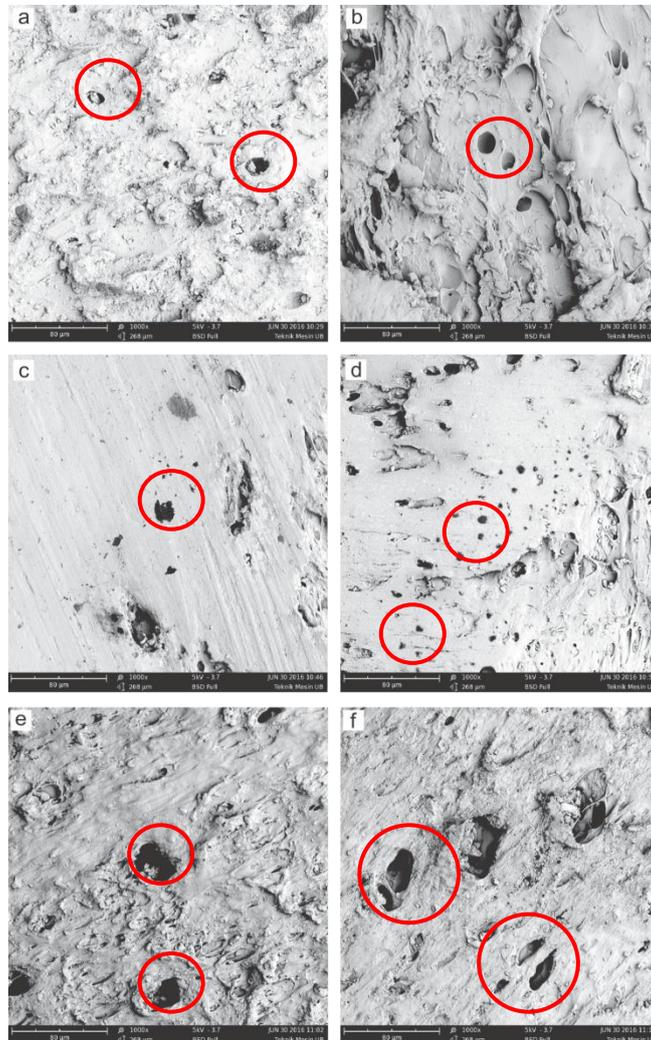


Figure 3. SEM results for *poly (methyl methacrylate-co-styrene)* (a) without the addition of styrene, (b) addition of 10 wt%, (c) the addition of 20 wt%, (d) addition of 30 wt%, (e) the addition of 40 wt%, and (e) the addition of 50 wt% of styrene

Porosity emerged as a result of the rudimentary mixing process between powder and liquid components. It resulted in some areas that contain more resin monomer than others. During the polymerization process, such areas shrank more than the other regions and tend to produce shrinkage cavities [6]. The use of the fluid resin technique with the layer-by-layer system also can cause the synthesis of the copolymer. It was because of the air trapped during the gradual process of the resin casting which also caused the porosity that can arise. The presence of the porosity or cavities on the synthesized copolymers can affect the mechanical properties of the copolymer. The increasing number of cavities that appear led to the decreasing mechanical properties of the polymer [11]. Table 2 and Figure 4 show that the addition of styrene groups to the main chain of the copolymer was able to lower its water absorption performance. The amount of water absorption of denture base depends on the degree of hydrophobicity and porosity [16]. Methyl methacrylate contains carboxyl groups that can

form hydrogen bonds with water molecules. With the addition of styrene, copolymer groups can bring hydrophobic interactions with aromatic rings [17]. The water absorption capacity of a denture base not only depends on the polarity of the constituent materials, but diffusion mechanisms also play a role in the process of water molecule entry into the polymer chain [11]. According to the copolymer SEM results shown in Figure 3, the increasing value of water absorption in copolymers with the addition of styrene monomer content of 30 wt% and 50 wt% also caused the cavities that appeared on both additions. The presence of the cavity made it easier for the water molecules to extend into the copolymer which had been synthesized so as to increase the capacity of its water absorption.

Table 2. The effect of the styrene addition on water absorption capacity of the copolymer sample

The styrene addition into the copolymer sample (wt%)	The average water absorption value (mg/mm ³)
0	6.54
10	4.25
20	3.50
30	4.10
40	2.40
50	2.95

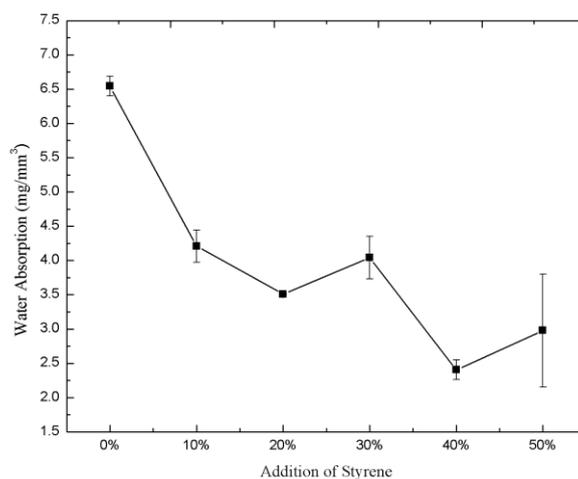


Figure 4. The effect of styrene addition on water absorption of the copolymer sample

Table 3. The effect of the styrene addition on the copolymer sample solubility

The styrene addition into the copolymer sample (wt%)	The average water absorption value (mg/mm ³)
0	1.87
10	0.99
20	0.9
30	1.25
40	0.42
50	1.52

Table 3 and Figure 5 demonstrated that the addition of styrene to the main chain of the copolymer was able to lower the value of its solubility. The increased value of solubility in the addition of 30

wt% and 50 wt% of styrene indicated a higher level residual monomer when compared to copolymers with the addition of 10, 20, and 40 wt%. The value solubility in the denture base had a correlation with the possible emergence of residual monomer.

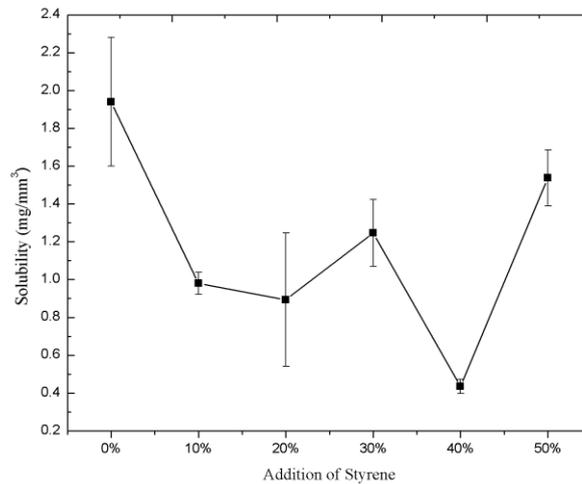


Figure 5. The effect of the styrene addition on the solubility of the copolymer sample

There is a correlation between residual monomer and water absorption [16] which would increase the value of absorption and solubility of the residual monomer. Such indication would also be correlated with the results of the mechanical testing. A relation between residual monomer and mechanical properties was also obtained. The residual monomer acted as a plasticizer tended to degrade the mechanical properties of denture base materials [17]. Flexural testing was done because it was considered as most suitable for comparing the denture base materials. The test can reflect the complex pressures that occur during the process of chewing and provides an indication of the strength of the material. Figure 6 shows the effect of the styrene monomer addition on the value of flexural strength and flexural modulus copolymer of *poly (methyl methacrylate-co-styrene)* was successfully synthesized.

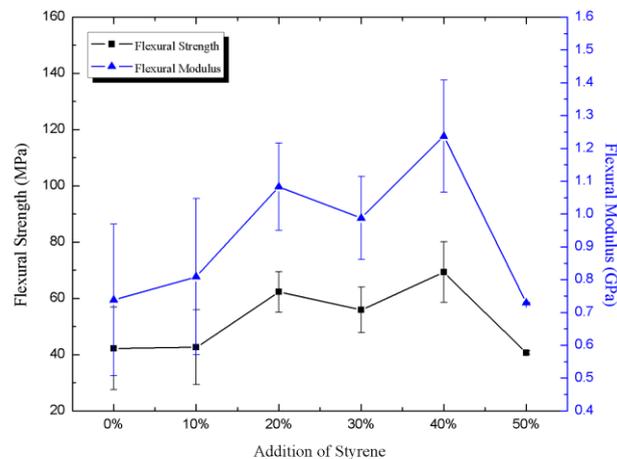


Figure 6. The effect of the styrene addition to copolymer *poly (methyl methacrylate-co-styrene)* flexural strength and flexural modulus

Figure 6 indicates that the obtained value of flexural strength and flexural modulus copolymer of *poly (methyl methacrylate-co-styrene)* increased together with the addition of styrene. However, there was a decline in the values of flexural strength and flexural modulus when given the addition of styrene 30 wt% and 50 wt%. Several factors influence the flexural properties of the acrylic resins, such as residual monomer, water absorption, and porosity [18]. It was consistent with the results of water absorption test shown in Figure 4 and the solubility shown in Figure 5. If the water absorption test result was related to its solubility, an indication of residual monomer affects the flexural strength of a denture base because of its plasticizing properties [19]. The plasticizing parts of such plasticizing properties caused the decreased mechanical properties of the polymer. An indication of residual monomer also caused porosity that can affect the mechanical properties [20]. It was consistent with the presence of cavities which were visible on the SEM test results shown in Figure 3.

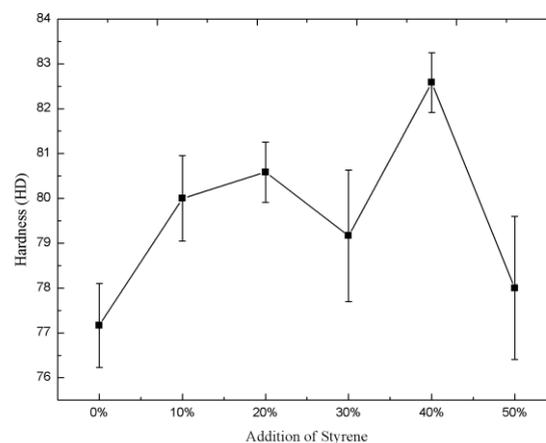


Figure 7. The effect of the styrene addition on the copolymer *poly (methyl methacrylate-co-styrene)* hardness

Table 4. The effect of the styrene addition on the hardness of the copolymer sample

The styrene addition to the copolymer sample (wt%)	The average hardness value (HD)
0	77.3
10	80.0
20	80.5
30	79.2
40	82.5
50	78.0

Their benzene rigid group was added into the polymer main chain, along with the addition of styrene monomer, and then the hardness of the modified acrylic compound would show an increasing trend [21]. The hardness values were also associated with the residual monomer in the acrylic denture base resin as shown in Table 4 and Figure 7. The hardness values also decreased along with the increasing value of water absorption. The lessened hardness in the addition of 30 wt% and 50 wt% had a common trend with the values of water absorption, solubility, flexural strength, and flexural modulus.

The results of the test were then compared with the standard *ANSI/ADA Specification No. 12 (ISO 1567) for Denture Base Resin* to determine whether or not the synthesized copolymer fulfills the requisites for denture base material. In Table 5, a comparison of the physical and mechanical

properties of copolymers that had been synthesized with the physical and mechanical properties that are necessary to become a denture base material.

Based on Table 5, it was found that the addition of styrene copolymer with a composition of 40 wt% was the closest composition to the necessary requirements determined by *ANSI/ADA Specification No. 12 (ISO 1567) for Denture Base Resin*.

Table 5. Mechanical properties of the copolymer and denture base material specifications

Properties	ISO 1567	Addition of the styrene monomer					
		0%	10%	20%	30%	40%	50%
Water Absorption ($\mu\text{g}/\text{mm}^3$) maximum	32	6.54	4.20	3.50	4.04	2.40	2.97
Solubility ($\mu\text{g}/\text{mm}^3$) maximum	1.6	1.94	0.97	0.89	1.24	0.43	1.53
Flexural Strength (MPa) minimum	65	42.22	42.61	62.29	55.88	69.33	40.73
Flexural Modulus (GPa) Minimum	2.0	0.73	0.80	1.08	0.98	1.23	0.72
Hardness (HD)	-	77.16	80	80.58	79.16	82.58	78

4. Conclusion

The addition of styrene copolymer *poly (methyl methacrylate-co-styrene)* led to a decrease in the value of water absorption and solubility, an increasing value of flexural strength and flexural modulus, and an increasing value of its hardness. The copolymers with the addition styrene of 40 wt% has physical and mechanical properties that are close to the requirements of denture base materials.

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