



EFFECTS OF CROSS-LINKING AGENTS AND RADIOPACIFYING FILLERS ON DEGREE OF CONVERSION AND VOLUMETRIC SHRINKAGE OF DENTURE BASED METHACRYLIC RESINS

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Development of experimental dental prostheses formulations based on methacrylic resins. The study of effects, on the degree of conversion (DC) and volumetric shrinkage (VS) of four crosslinking agents: DEDGMA, TEGDMA, TETRAEGDA and TMPTA and four radiopacifying mineral fillers: ZrO₂, TiO₂, SrO and BaO₂. The experimental resins are compared to commercial products.

The (DC) determination of the experimental and commercial resins was carried out by FTIR in ATR mode. The (VS) was determined experimentally by the Archimed's method.

Chemical structure and weight content of crosslinking agents affected (DC) and (VS). (DC) and (VS) increased with the crosslinking agent chain length and weight contents. Additionally, whatever filler contents and metal nature, (DC) values remains $\geq 99.5\%$, in accordance with the standards required for residual monomers level tolerated in dental prostheses ($<0.45\%$). (VS) values varied between 4.8 and 10.8%. For two commercial resins, (DC) values were less than 99% while (VS) was in accordance with the standards (5–6%): 6.2% for Major base and 4.3% for Hiflex H.



INTRODUCTION

The functional failure of human organs such as teeth is overcome by substitute biomaterials able to fulfill the initial organic role. Polymethyl methacrylate (PMMA) is a biocompatible polymer that adapts to dentures and its intolerance, caused by allergies, is often rare. However, when they occur, the trigger allergen should be found in the raw materials of the prosthesis.^{1,2} Thus, patch tests have mainly detected the reactions to the initiator, benzoyl peroxide (BPO), and the inhibitor: hydroquinone.^{3,4} In addition, the two main monomers that make up dental resin – methyl methacrylate (MMA) and the crosslinking agent – are the main allergens.^{5,6} Allergic reactions to

methacrylic prostheses^{7,8} have been explained by the presence of residues of these monomers, released into the oral environment. According to studies,^{9,10} when the amount of residual monomer in saliva is high, it can cause irritation, inflammation, hyper sensitization and allergic response of mucosal tissues. Other studies^{11,12} have also revealed the influence of the residual monomer level on the physico-chemical and mechanical properties of dental materials, which could alter the wear resistance, hardness and discoloration reactions. Therefore, a low degree of conversion would cause allergic reactions and promote bacterial growth. Thus, the level of residual MMA in the final material depends on the (DC).^{13,14} It has been demonstrated^{15,16} that during

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the radical polymerization of resins the gradual transformation of material into a rigid polymer network is generally accompanied by a volumetric shrinkage (VS), implying a change of the free volume in the formed macromolecular network. (VS) remains one of the major drawbacks leading to clinical failure of prosthesis placement and directly influences the (DC) of material. A direct correlation has been observed between these two properties.¹⁷⁻¹⁹ These organic resins, being generally transparent to X-rays, various radiopacifying agents, consisting of high atomic numbers atoms containing salts or oxides such as barium, strontium, zirconium or titanium are incorporated into the polymer matrix, in order to make it radiopaque.²⁰ The nature and concentration of these radiopaque additives determine the material's radiopacity level. The latter is currently required and formally recommended by the International Organization for Standardization (ISO), in the field of plastics technology and in medical applications.²¹⁻²³

The current study aimed to elaborate a reliable denture based resin methacrylic material by finding the right formulation to assess the residual MMA leaching from methacrylic resin materials by raising the degree of conversion and minimizing the volumetric shrinkage in order to maintain oral health from molecules released in the mouth. The effect of varying different crosslinking agents and radiopacifying mineral fillers, at different contents by weight on (DC) and (VS) of experimental thermo-polymerizable methacrylic resins were

carried out and compared to commercial denture formulations.

EXPERIMENTAL

Materials: The MMA monomer was used without purification (Aldrich chemical Co., Milwaukee, USA). In each sample, 1 wt.% Benzoyl peroxide (BPO) and 1 wt.% Dimethyl Amino Ethyl Methacrylate (DMAEMA) initiator and co-initiator were introduced, respectively. 2 wt.% of dioctyl phthalate (DOP) was also added as a plasticizer. Different crosslinking agents and microscopic size radiopacifying microfillers, Tables 1 and 2, have been added. A low molecular weight oligomer: PMMA, synthesized in laboratory by the conventional radical polymerization, from the mixture of an adequate amount of MMA and BPO in ethanol at a temperature of 80°C during 1 hour under an inert atmosphere, was also added. The PMMA's molecular weight was determined by viscometry^{24,25} using a standard Ubbelohde brand SCHOTT capillary viscometer, and the value of the average molecular mass was found to be: $M = 128494.9$ (g/mol).

Experimental methacrylic resins elaboration

Based on standard composition of marketed dental resins, which are in form of liquid and powder mixed at time of use,²⁵ Table 3 rallied composition of liquid and powder phases of elaborated methacrylic resins.

The experimental methacrylic resins elaboration was carried out by carefully mixing liquid and powder phase at volume ratio of (2/3), until homogeneous pasty texture was obtained.

The obtained pasty resin was divided into two parts: one part was reserved for characterizations before polymerization, the other was placed in a specific muffle (Fig. 1), containing plaster with a cavity corresponding to a footprint. The muffle was then sealed with a clamp, compressed, and placed in a bath thermostatically controlled at 90°C, heated and maintained at this temperature for 45 minutes. At the end of the polymerization process, the muffle was removed from the bath and unmolded cold (Fig. 1).

Table 1

Chemical structures of crosslinking agents used in experimental methacrylic resins formulations

Nomenclature	Chemical structure
Di-ethylene glycol dimethacrylate (DEGDMA)	
Triethylene glycol dimethacrylate (TEGDMA)	
Tetraethylene glycol diacrylate (TETRAEGDA)	

Table 1 (continued)

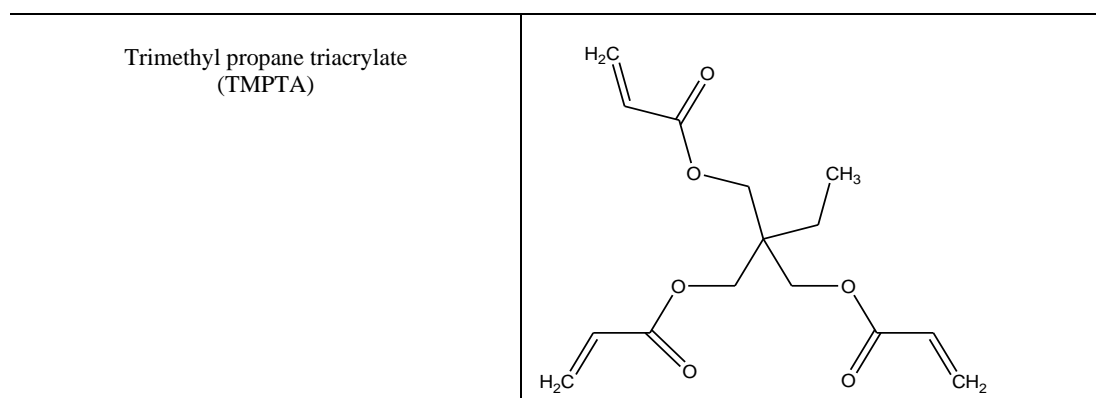


Table 2

Radiopacifying microfillers used in experimental methacrylic resins formulations

Mineral microfiller	Metal atomic number (Z)	Metal mass number (A)
TiO ₂	22	47.86
SrO	38	87.62
ZrO ₂	40	91.22
BaO ₂	56	137.33

Table 3

Chemical composition of experimental methacrylic resins formulations

Powder	Liquid
Prepolymer (PMMA): 4.2g	Monomer (MMA): 2 ml
Initiator ^{**} : PBO (1%)	Crosslinking Agents ^{**} : 2% – 4% – 6% <ul style="list-style-type: none"> • DEGDMA • TEGDMA • TETRAEGDA • TMPTA
Fillers [*] : ZrO ₂ ; TiO ₂ ; BaO ₂ ; SrO, weight contents: 1.5–2.5–3.5%	Co-initiator ^{**} : DMAEMA (1%)
	Plasticizer [*] : DOP (2%)

* Radiopacifying fillers and plasticizer amounts were determined relatively to the reaction mixture's total mass.

** Crosslinking agents, initiator and co-initiator's amounts were determined based on MMA's volume.



Fig. 1 – Muffle containing a methacrylic resin after polymerization.

Table 4

Characteristics of commercial dental methacrylic resins

Commercial name	Manufacturer	Composition
Hiflex – H Ultra high impact heat cured denture base	PREVEST DenPro, (India)	Powder: PMMA Liquid: MMA
MAJOR BASE ₂₀ Heat-proceed polymer powder and liquid	MAJOR PRODOTTI DENTARI S.p.A. (Italy)	Powder: PMMA Liquid: MMA

For comparison, two commercial dental methacrylic resins were studied, and their characteristics are depicted in Table 4.

Methods

Determination of the degree of conversion by FTIR-ATR

(DC) determination of experimental and commercial methacrylic resins was carried out using an infrared spectroscopy apparatus FTIR Nicolet type, 360 Avatar 360 FTIR spectroscopy in ATR mode type Pike miracle ATR, Diamond / ZnSeW / Pike Technology. The FTIR spectra exploitation^{26,27} of each sample, before and after polymerization, and using empirical relation (1),¹⁷ allowed us to determine the (DC) experimental values of each sample.

$$DC(\%) = \left[1 - \frac{\left(\frac{P_1}{P_2} \right)}{\left(\frac{P_1'}{P_2'} \right)} \right] \times 100 \quad (1)$$

where: P_1 and P_1' represent, respectively, the peak ($C = C$) area or height of the methacrylate groups, located around $1,638 \text{ cm}^{-1}$ after and before polymerization. P_2 and P_2' represent respectively the area or height of the peak ($C = O$) of the methacrylate groups after and before polymerization.

Determination of volumetric shrinkage by Archimed's method

(VS) determination of experimental and commercial methacrylic resins was carried out according to volumetric dilatometric methods^{28,29} based on Archimed's method.^{30–33}

The volumetric shrinkage (V_s) can be determined as follows:^{34, 35}

$$V_s = (V_{bp} - V_{ap}) \quad (2)$$

V_{bp} : Sample volume before polymerization; V_{ap} : Sample volume after polymerization.

The volumetric shrinkage variation ($\Delta V/V$) (%) is calculated by:

$$(\Delta V/V) = [(V_{bp} - V_{ap}) / V_{bp}] \times 100 \quad (3)$$

Before polymerization, volume and density of experimental and commercial sample were determined. Each sample was then placed in a thermostated bath and polymerized under the same conditions described above. At

the end of reaction, the obtained samples were weighed using an electronic balance and their volumes and densities were measured. The ($\Delta V/V$) values of each experimental and commercial resin were calculated by means of relation (3).

RESULTS AND DISCUSSION

Effects of crosslinking agents chemical structure and weight contents on (DC) and (VS) of experimental and commercial dental resins

(DC) and (VS) values of commercial and experimental samples containing 0% fillers are depicted in Tables 5 and 6. Figures 2 and 3 show the variation of (DC) and (VS) as a function of crosslinking agent weight contents, respectively. It can be noted that for a given crosslinking agent, (DC) and (VS) rise with increasing weight content. This increase is more pronounced in the case of TETRAEGDA. In fact, with a high weight content, the presence of large quantities of crosslinkable double bonds results in a denser network formation and hence a high degree of crosslinking, which results in a significant (DC) value. We also noted that for a given weight content, (DC) and (VS) rise with increasing crosslinking agents chain length. This result can be linked to the chain flexibility which increases with its length. The molecular chains are therefore less compact which facilitate the double bonds accessibility resulting in a high (DC) value. As a result, the network shrinks and contracts, causing the increasing of (VS). Additionally, samples containing 6% of crosslinking agent exhibit the highest (DC) and (VS) values. However, this quantity remains quite high compared to that indicated in commercial resins (2–4%).²⁶ However, it can be seen from Fig. 2 that (DC) values of TMPTA containing samples decrease as its weight content increases. This

behavior is in contradiction with that observed with the other three dimethacrylates studied. This result can be explained by the TMPTA chemical structure which contained short triacrylate functions (Table 1). So during propagation, chains mobility and flexibility were restricted and double bonds was less accessible, causing free radicals occlusion and hence decreasing (DC) with the increasing of MPTA weight contents. For comparison, results showed that commercial resins

(DC) values (Table 6), are higher than those of the experimentals containing 0% fillers (Table 5) with the exception of samples containing 4 and 6% TETRAEGDA whose (DC) values are closed to commercials. Moreover, experimental resins (VS) values are clearly higher than those of commercial resins, with the exception of samples containing 2% DEGDMA (5.01%) and TETRAEGDA (5.13%) crosslinking agents.

Table 5

(DC) (%) and (VS) (%) values of experimental methacrylic resins containing 0% fillers at different crosslinking agents

Crosslinking agent Weight content (wt.%)	DEGDMA		TEGDMA		TETRAEGDA		TMPTA
	(DC)	(VS)	(DC)	(VS)	(DC)	(VS)	(DC)
2	21.54	5.01	24.86	5.13	48.52	9.8	48.2
4	32.37	7.6	46.82	9.73	72.14	14.4	38.3
6	39.88	9.45	58.65	12.3	79.98	16.09	35.05

Table 6

(DC) (%) and (VS) (%) values of commercial methacrylic resins

Commercial resins	(DC) (%)	(VS) (%)
Hiflex-H	85.57	4.34
Major Base	98.96	6.24

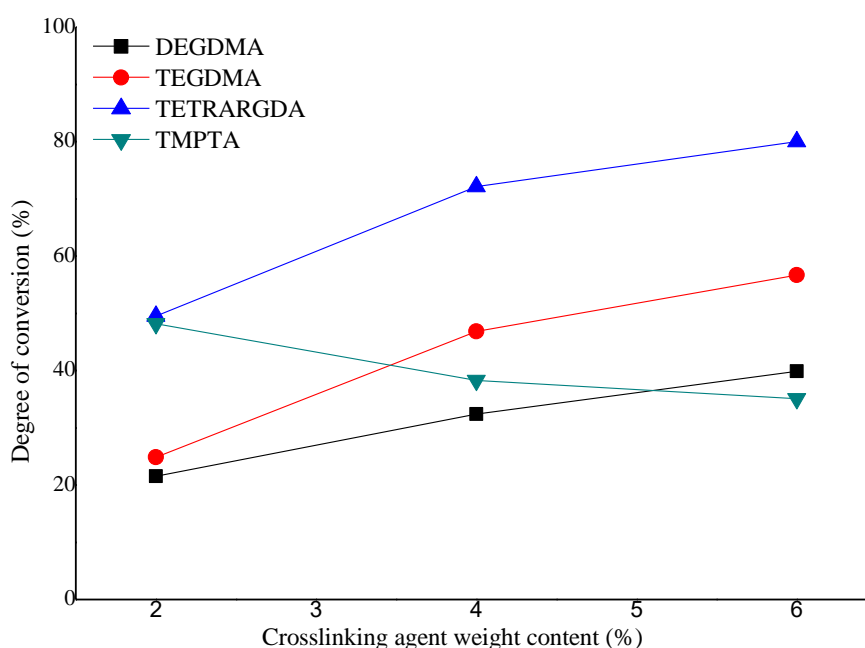


Fig. 2 – Degree of conversion vs crosslinking agent weight content of experimental resins containing 0% fillers with different crosslinking agents.

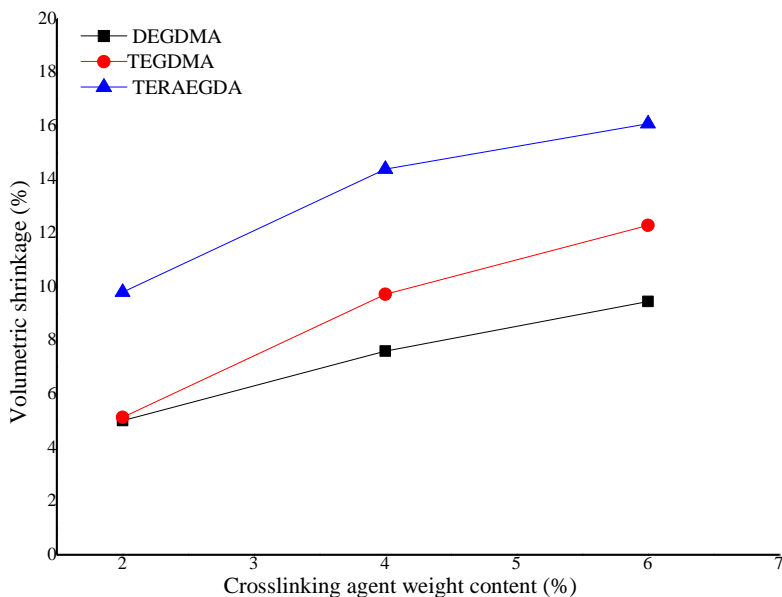


Fig. 3 – Volumetric shrinkage vs crosslinking agent weight content of experimental resins containing 0% fillers with different crosslinking agents.

Table 7

(DC) (%) values of experimental methacrylic resins containing 4% of TETRAEGDA at different radiopacifying fillers weight contents

Mineral fillers	Weight content (%)		
	1.5	2.5	3.5
TiO ₂	99.88	99.85	99.82
SrO	99.78	99.69	99.57
ZrO ₂	99.62	99.55	99.45
BaO	99.50	99.45	99.40

Effects of radiopacifying fillers nature and weight contents on (DC) and (VS) of experimental methacrylic resins

a. Effect on degree of conversion (DC)

(DC) values of experimental resins containing 4% of TETRAEGDA, at different fillers with different weight contents, are listed in Table 7. We opted for TETRAEGDA at a weight content of 4% because it presented the best results. Figures 4 and 5 illustrated, respectively, (DC) variation as a function of weight contents fillers and a comparative histogram with commercial resins. It is noted that all the investigated materials showed consisted (DC) values greater than 99%. This very promising result was in agreement with published studies²⁶ since the threshold of residual monomer tolerated in dental prosthesis 0.45%. As shown in Fig. 4, we

noted that (DC) values decrease with increasing of weight content fillers. Indeed, the incorporation of inorganic fillers could restrict chains mobility due to the volume occupied by fillers in the network, implying the slowing down of free radicals mobility. Additionally, it should be noted that for given filler studied, (DC) varied linearly as a function of weight content. This linear variation was in agreement with the literature.¹⁷ For a given filler weight content, it can be seen that (DC) values decrease when metal atomic number (Z) containing fillers increases (Table 2). Indeed, although the weight content was the same, fillers containing the heaviest and bulky metal occupied a larger volume in the network. It can also be seen from (Fig. 5), that experimental resins presented higher (DC) values than those of commercial. It should be noted that (DC) value of Hiflex H resin was lower than that of Major base resin.

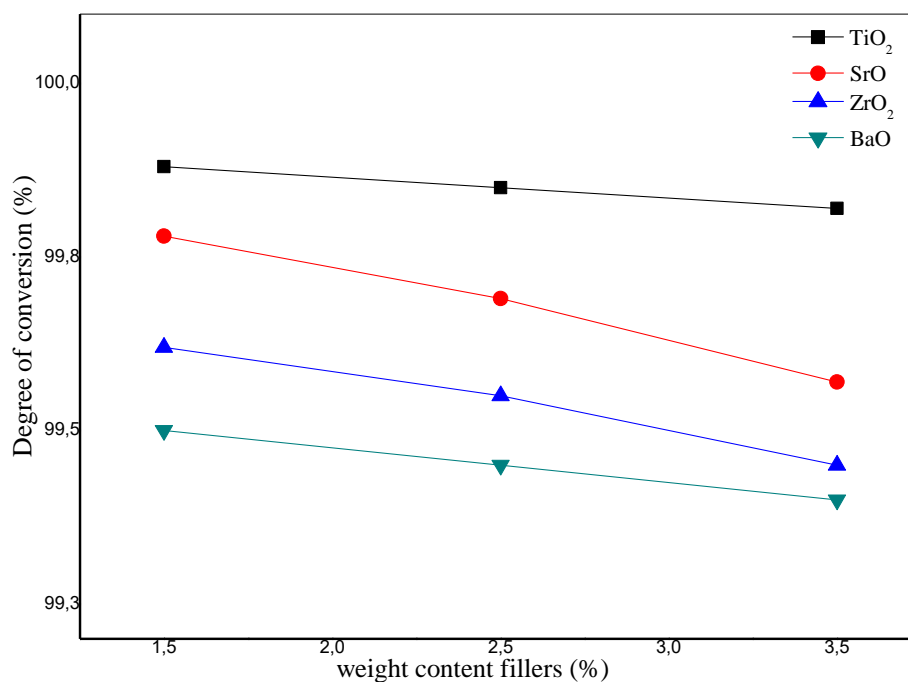


Fig. 4 – Degree of conversion vs weight content fillers of experimental resins containing 4% of TETRAEGDA at different mineral fillers.

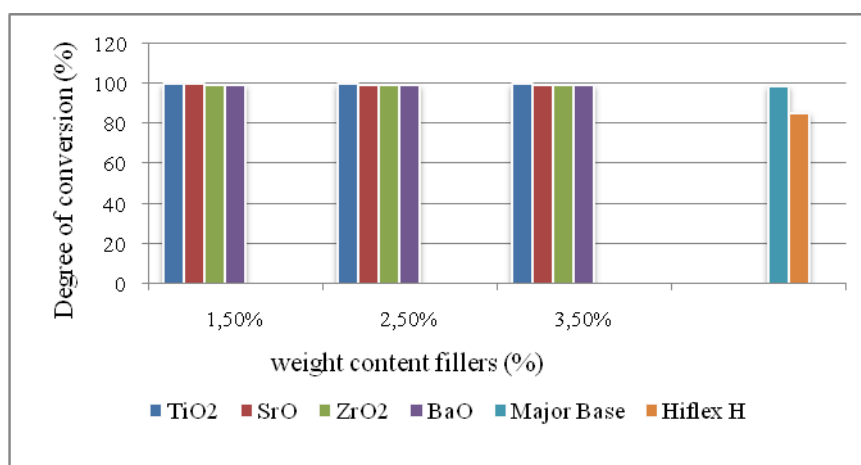


Fig. 5 – Histogram of (DC) vs weight content fillers of experimental resin as a comparison with commercial methacrylic resin.

Table 8

Density values before (D_{bf}) and after (D_{af}) polymerization and (VS) (%) values of experimental resins at different mineral fillers weight contents

Mineral fillers	1.5 %			2.5 %			3.5 %		
	D_{bf}	D_{af}	(VS)	D_{bf}	D_{af}	(VS)	D_{bf}	D_{af}	(VS)
TiO ₂	1.017	1.044	10.80	1.009	1.036	9.67	1.007	1.033	8.45
SrO	1.006	1.076	9.53	1.004	1.036	8.16	1.005	1.054	6.95
ZrO ₂	1.006	1.009	7.53	1.009	1.003	6.76	1.010	1.001	6.00
BaO	1.005	1.008	6.38	1.013	1.008	5.28	1.036	1.009	4.91

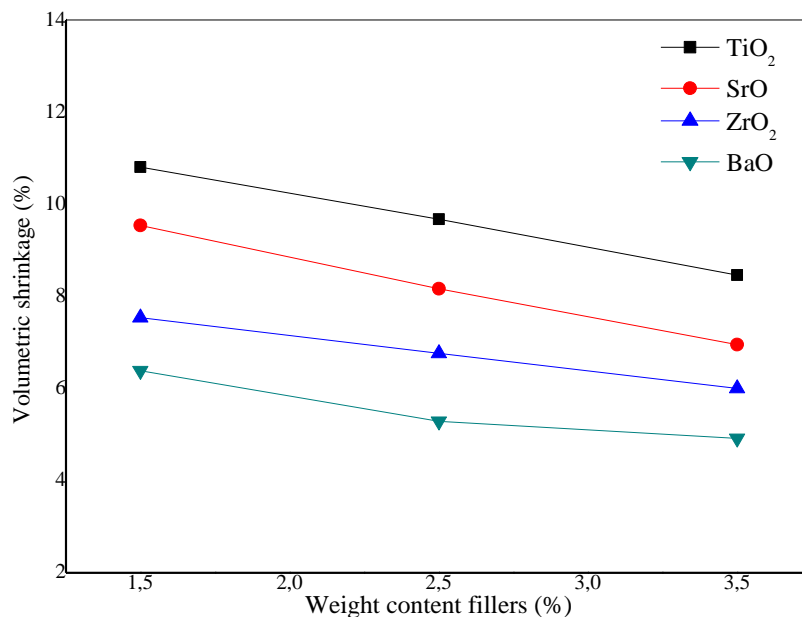


Fig. 6 – Volumetric shrinkage vs weight content fillers of experimental resins containing 4% of TETRAEGDA at different mineral fillers.

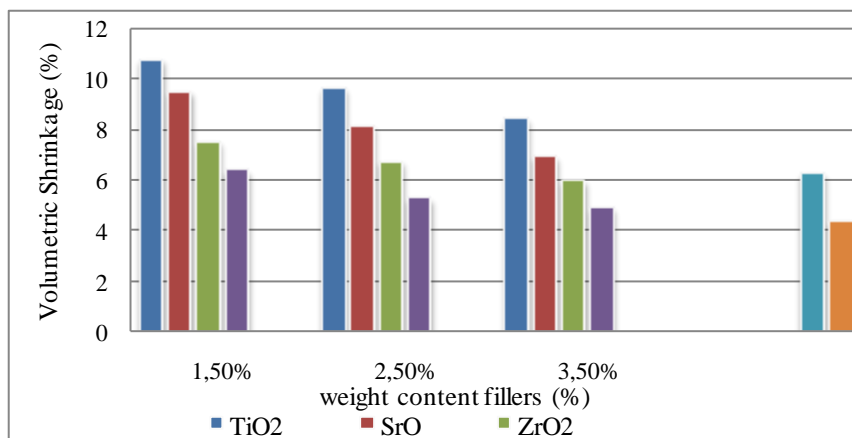


Fig. 7 – Histogram of volumetric shrinkage vs weight content fillers of experimental resin as a comparison with commercial methacrylic resin.

b. Effect on volumetric shrinkage (VS)

Table 8 lists experimental densities values before (D_{bf}) and after (D_{af}) polymerization and (VS) values of the experimental resins containing 4% of TETRAEGDA, at different mineral fillers weight contents. Figures 6 and 7 illustrated, respectively, the variation of (VS) as a function of fillers weight content of experimental resins and the comparative histogram with commercial resins.

We noted that regardless of the sample, density values are intermediate to those of MMA (0.944) and PMMA (1.18) which suggested that Archimed's method can be a reliable method for the determination of methacrylic resin density experimentally. From Fig. 6, we noticed that for a

given filler, an increase of filler weight contents was accompanied by a linearly decrease of (VS). This decrease was more pronounced compared to that observed in (DC) study on Fig. 4. This predictable result was in agreement with the results of other.¹⁷ Indeed, the incorporation of mineral fillers occupying a large volume in organic matrix resulted in restriction of macromolecular chains mobility and minimized the chain segments movement. The metal size has also an impact in the occupation of three-dimensional network free volume which has the effect of countering volumetric shrinkage. In Table 8, it can be seen that (VS) values varied from 4.91% to 10.8%. The percentage of (VS) tolerated in dental prosthesis is

(5–6%).²⁶ However, according to Table 8, ZrO₂ and BaO content exhibited (VS) values in this range. Moreover, there was a marked decrease in (VS) with increasing the metal atomic number (Z) containing fillers. Comparatively, as shown in Fig. 7, (VS) values of commercial resins were lower than those of experimental resins. Hiflex H resin has a (VS) value less than 5%.

CONCLUSIONS

The purpose of this study was to enhance (DC) and minimize (VS) in dental prosthesis three-dimensional network to obtain a material which respects standards in terms of residual monomers released but also to find the right formulation to elaborate a reliable denture based resin methacrylic material as regards the preservation of health from molecules released in the mouth. In this work, the method adopted was to vary the nature and contents of crosslinking agents and mineral microfillers and evaluated the effect on degree of conversion and volumetric shrinkage. Regarding the finding in this study, this investigation demonstrated that all data obtained from the elaborated methacrylic resins based on standard commercial dental resins formulations exhibited (DC) values > 99%. Thus, toxic monomer residues released in oral cavity are negligible. However, our results revealed that (VS) values remained quit high in comparison with standards imposed excepted for experimental materials containing BaO (2.5 and 3.5 weight %) and ZrO₂ (3.5 weight %) mineral fillers, which showed the lower (VS) values. Further research on experimental denture based material performance in clinical application needs to be considered.

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