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Evaluation of Surface hardness of Denture Base Acrylic Resin Modified with Different Techniques

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Abstract

Aims: Evaluation of the surface hardness of heat-treated acrylic resin after modifying it with three different techniques. **Materials and Methods:** Heat cured acrylic resin was modified by: (a) The copolymerization of acrylic resin with 5% and 10% of acrylic acid (AA), (b) The addition of 5% and 10% thermally activated zinc oxide (ZnO) and (c) The chemical bonding or engagement of Zinc ions into the polymer chain by an organic link, zinc diacrylate (ZDA) in 5% and 10%, to get a copolymer. The acrylic specimens have dimensions of (30, 15 and 3) ± 0.2 mm. Surface hardness was determined using a Durometer (Shore D) hardness tester. **Results:** There was general increase of the surface hardness of the experimental (modified) groups. A statical significant increase in the hardness of both acrylic groups modified by 10% ZnO and 10% ZDA compared to the control group and the remaining modified samples. **Conclusion:** Two techniques had significantly improved the hardness of heat cured acrylic resin; either by adding 10% by weight of thermally activated ZnO or by copolymerizing it with 10% by weight of ZDA to get poly (methyl methacrylate -co-zinc acrylate) copolymer.

الخلاصة

الأهداف: تقييم صـــــلادة الســـطح للراتنج الأكريليك المعالج حراريا بعد تعديله بثلاث تقنيات مختلفة. **المواد وطرائق العمل:** تم تعديل الراتنج الأكريليك المعالج حراريا عن طريق: (أ) البلمرة المشـــتركة لراتنج الأكريليك مع 5٪ و 10٪ من حمض الأكريليك (AA) ، (ب) إضـــافة 5٪ و 10٪ ZnO المنشـــط حرارياً و(ج) الترابط الكيميائي أو ارتباط أيونات الزنك في سلسلة البوليمر بواسطة رابط عضوي ، ثنائي أكريلات الزنك (ZDA) بنسبة 5٪ و 10٪ ، للحصول على بوليمر مشترك. عينات الأكريليك لها أبعاد (30 ، 15 ، 3) ± 0.2 مم. تم تحديد صلادة السطح باستخدام جهاز اختبار الصلادة (Shore D Durometer). **النتائج:** كان هناك زيادة عامة في صلادة السطح للمجموعات التجريبية (المعدلة) مقارنة بمجموعة التحكم (غير المعدلة). زيادة معنوية إحصـــائية في صـــلادة مجموعتي الأكريليك المعدلة بنسبة 10٪ ZnO و 10٪ ZDA مقارنة بمجموعة التحكم والعينات المعدلة المتبقية. **الاستنتاجات:** تم تحسين صلادة السطح لراتنج الأكريليك المعالج حراريا المعدلة بإضافة ZnO بشكل كبير في تقنيتين؛ إما بإضافة 10٪ بالوزن من ZnO المنشط حرارياً أو عن طريق البلمرة المشتركة مع 10٪ من وزن ZDA للحصول على بوليمر مشترك بولي (ميثيل ميثاكريلات- كو- زنك أكريلات).

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INTRODUCTION

Several studies were conducted on using metal oxides to enhance denture base resin. Some have found a significant improvement in the properties of acrylic [1-15], other didn't find the desired result [16]. The important factor that plays a major role in the successful enhancement of the properties of the particulate filled polymer compounds is the strong adhesion of the filler to the interface of the polymer matrix [17, 18]. Inorganic reinforcing fillers typically display high surface energy due to the ionic hydrophilic nature. However, the waterproof polymer does not wet out or react with the filler due to the difference in surface energies. Therefore, different ways had been demonstrated to recover surface wetting, compatibility and holding between inorganic filler particles and organic matrix materials. Among these methods, silanation is most commonly used for surface modification to get particulate filled acrylic composite having improved properties over pure acrylic [11,19-25]. Other researchers achieved a good adhesion of fillers with acrylic resin matrix by modifying the fillers' surfaces with PMMA. They proved that such modification can greatly improve resin's transverse mechanical properties [26]. Treatment of fillers with a variety of bonding agents or primers preceding to admixing with the polymer in order to create a strong interphase between structural medium and the resin matrix reported an improvement of the acrylic resin properties for provisional fixed restorations [9,19,27].

ZnO can be considered as a promising metal oxide which can be used to alter the biomaterial for denture bases [28-35]. It is used as a radio-opaque material to make acrylic resin visibility in x-rays better [36]. It is also utilized as a pigment to develop aesthetics of denture acrylic. [37, 38] Moreover, ZnO was found to increase acrylic hardness [39] and participate in increasing acrylic thermal conductivity and strength and decreasing its roughness [15].

Hardness is defined as the material's resistance to a permanent indentation [40]. Testing hardness has been commonly used as a reference indicating the degree of conversion of resins, the mechanical quality of polymers [41-47] and the prosthesis longevity because the higher the hardness is, the higher the wear resistance [48-50]. Therefore, in the present study, the efficiency of the above-mentioned ways of acrylic resin modification was evaluated in term of preservation or improvement of surface hardness. The null hypothesis was that these modifying procedures do not diminish the hardness of the heat cured acrylic resin.

MATERIALS AND METHODS

According to the research layout which was determined by previous preliminary tests, the samples of heat cured acrylic resin (Prothyl press EVO 162/ Zhermack® technical Italy) were divided into seven groups (Table 1):

Table (1): Heat cured acrylic resin groups.

Group	Description
G1	Unmodified acrylic resin samples (control group)
G2	Modified acrylic resin samples by 5% AA
G3	Modified acrylic resin samples by 10% AA
G4	Modified acrylic resin samples by 5% ZnO
G5	Modified acrylic resin samples by 10% ZnO
G6	Modified acrylic resin samples by 5% ZDA
G7	Modified acrylic resin samples by 10% ZDA

ZnO powder was thermally activated at 900°C for 2 hours [51], milled using a vibratory disc mill and sieved with a 25µm sieve. Zinc Diacrylate (ZDA) was synthesized by the following procedure; ZnO (8.14 g, 0.1 mol) was mixed with 33 ml deionized distilled water. Then (14.4 g, 0.2mol) acrylic acid was added to the mixture. The reaction was carried out at room temperature for 24 hours to obtain zinc diacrylate as insoluble precipitate which was filtered, dried and milled. The resulted powder was examined by FT-IR spectroscopy to be characterized. It was then kept in a sealed glass vial until use. All the specimens of modified and unmodified acrylic resin materials (n=35; five for each group) were processed in the conventional compression molding technique., trimmed and finished to fit the dimensions, (30 ± 0.2) mm long, (15 ± 0.2) mm wide and (3 ± 0.2) mm in height [52]. A detailed description of the used materials, treatment of the additives and preperation of the polymerized samples were explained in a previous article [53].

After polymerization, The specimens were stored in deionized distilled water at (37 ± 1) °C for (48 ± 2) hours for hydration and residual monomer release before measuring [54].

Surface hardness was assessed using Durometer hardness tester (Shore D, Shaw, Model: LD – YJ, China) for hard materials. It was fabricated according to American National Standard / American Dental Association (ANSI /ADA, 2002) [40]. Five measurements were recorded on different places of each single specimen and the mean value was calculated. Shore durometer is a dimensionless quantity because it measures the relative movement of the indenter.

IBM© SPSS© Version 19 was utelized to analyze the collected data.

RESULTS

The descriptive statistics of durometer Shore D hardness were represented in Table (2). This includes means, standard deviations, standard error of deviations, maximum and minimum values of hardness. The highest two mean values were recorded for G5 and G7 (86.80 and 87.92 respectively), while the lowest two mean values were recorded for G1 and G3 (85.44 and 85.64 respectively). One Way ANOVA test was represented in Table (3). Statistical significant difference exists between tested groups at p value ≤ 0.05.

Table (2): Descriptive statistics of surface hardness test.

Group	Mean (shore)	SD	SE	95% Confidence Interval for Mean		Minimum	Maximum
				Lower Bound	Upper Bound		
G1	85.44	0.58	0.22	84.37	86.51	81	92
G2	86.36	0.12	0.43	85.49	87.23	82	90
G3	85.64	0.85	0.37	84.89	86.40	83	90
G4	86.00	0.14	0.32	84.73	87.27	80	91
G5	87.80	0.08	0.42	86.82	88.68	83	91
G6	86.44	0.09	0.32	84.17	86.71	80	90
G7	87.92	0.07	0.36	87.17	88.67	84	91

Table (3): One Way ANOVA for surface hardness.

	Sum of Squares	Df	Mean Square	F	*P*
Between Groups	171.18	6	28.53	4.82	0.000
Within Groups	993.68	168	5.92		
Total	1164.86	174			

In table (3) and figure (1), one way ANOVA test showed that G2, G3, G4 and G6 didn’t have significant differences in comparison with the control material. While G5 and G7 groups have the highest hardness values (87.80 and 87.92 respectively) those are significantly different than all remaining samples. All the modified groups recorded mean values larger than that of the control group.

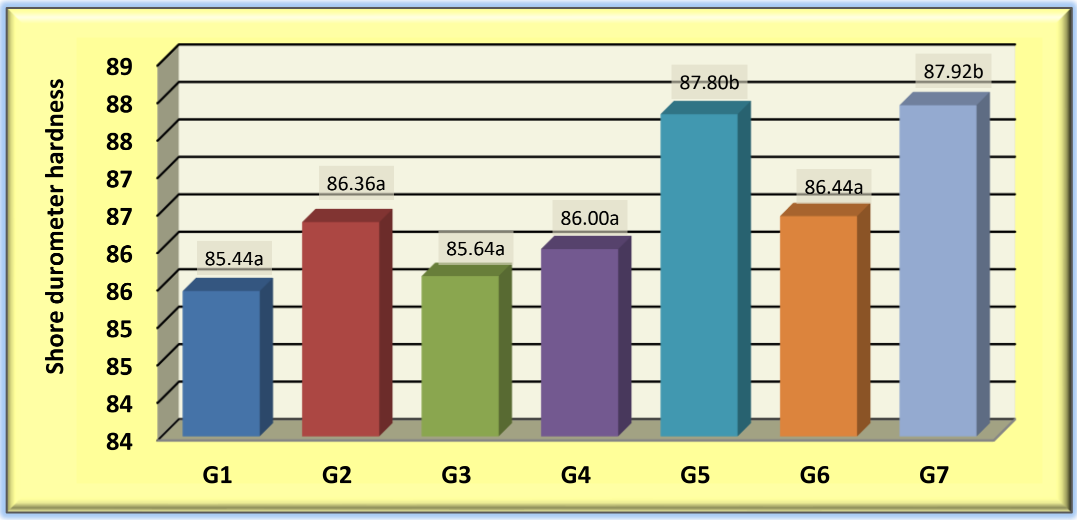

Figure (1): Duncan's multiple range test of durometer hardness.

DISCUSSION

Despite considerable efforts to improve the properties of acrylic resin denture base materials by incorporating different chemical modifiers, fibers, metals and particles, few have obtained promising results. Therefore, the objective of this work was to produce new different ways of modifying heat cured acrylic resin denture base material and to identify which method is better to improve denture base properties. In the preliminary study in our research series [53], five different ways of modification were tried; (a) The copolymerization of acrylic resin with acrylic acid, (b) The addition of thermally activated ZnO, (c) The chemical bonding or engagement of Zn ions into the polymer chain by an organic link (ZDA) to get a copolymer, (d) The addition of ordinary inactivated ZnO and (e) The addition of ordinary ZnO with AA. Fourier Transform Infrared Spectroscopy (FT-IR) was used to estimate degree of conversion, to characterize the materials under investigation and to compare between them. The study concluded that the addition of an ordinary ZnO or a thermally activated ZnO to acrylic resin appeared to be just as filling inserted within the inter-chain spaces without chemical bonding with the resin matrix. It also proved that synthesis and copolymerization of ZDA with MMA was the successful way to get a chemical engagement of Zn ions with the resin matrix.

The former study was followed by another one [55] customized to estimate the amounts of residual methyl methacrylate (MMA) in heat cured acrylic resin after its modification in the same mentioned ways. The study revealed that incorporation of 5% and 10% weight fraction from each of ZnO and ZDA into the acrylic resin significantly increased the amounts of residual MMA ($p \leq 0.05$), while modifying it by addition of AA had no effect on residual MMA amounts. Nevertheless, the residual MMA of all samples were lesser than ADA standardization Specification No. 12 [(40)].

To the best of the author's knowledge, no study has been carried out to assess hardness property of heat cured acrylic resins modified by the same techniques mentioned in this study. Therefore no comparison with other studies' results was performed. Moreover, since there is no interrnational specification for the hardness of denture base acrylic resin, the hardness values of the modified groups were compared with that of control one in the present study.

The results of the current study showed a general increase of the surface hardness of the experimental groups in comparison with the control group with a significant increase in both acrylic groups modified by 10% ZnO and 10% ZDA in comparison with the unmodified group and the remaining modified samples.

The hardness mean values of both acrylic resin groups modified by AA were greater than that of control. This is consistent with Al-Fahdawi (2009) and Abed (2010) [(56,57)] who copolymerized the heat cured acrylic resin with poly vinyl chloride (PVC) and stated that the produced copolymer was slightly harder than the unmodified material. Ayaz and Durkan [(58)] found enhancement of the mechanical characteristics of PMMA after its successful copolymerization with acrylamide monomer. The mechanical properties of acrylic resin are known to depend on ratios of powder/ liquid, the interface between the powder and the matrix and the crosslinking density of the polymer matrix. When the powder added to the liquid and mixed, the monomer dissolves and diffuses to the PMMA [(59)]. In the current study, the liquid monomer also dissolves the added acrylic acid particles (AA), so it is probable that addition of AA in different percentages may impact the acrylic properties differently.

The result showed the hardness of acrylic modified by 5% AA was greater than that of 10% AA group. This result displayed that a specific amount of AA (5%) could change the polymer matrix saturation for acrylic resin and when the amount of added AA was increased to 10%, a noticeable decrease in hardness occurred. This decrease may be clarified by the maximum saturation of the polymer matrix, which occurred by adding the 5% AA, and the excess monomer disturbed the crosslinked polymer structure.

Although ZnO is a relatively soft material with hardness of 4.5 on the Mohs scale [(60)], the addition of the prepared ZnO in 5% and 10% to PMMA increased hardness values in comarison with an unmodified group. These values increased depending on the raising of the filler concentration in the cured material from 5% to 10% by weight to become significant in 10% concentration. In inorganic-organic hybrid materials, the organic constituent usually accounts for flexibility of the composites whereas the inorganic constituent is responsible for hardness and mechanical impact resistance [20-22] and the hardness of heat cured acrylic resin increases with increasing the concentration of incorporated inorganic particles [61,62].

The size of filler particles in the polymer matrix has a great influence on the mechanical properties of particulate filled polymer composites [18]. The size of metal oxide particles should be small for proper handling [63] lesser prosity and reduced water sorption [36]. In this study the pretreated ZnO powder has micro/ nano sized particles ranging from (0.1090 − 1.0550µm) as determined by LASER Diffraction [53]. This metal oxide particle size was greatly smaller than that of powder resin particles (121.2µm) as mentioned by the manufacturer; therefore, they will fill the interstitials between polymer particles to give a heterogeneous mixture and will not force or displace the segments of polymer chain. In addition, since these particles are of micro/ nano sized, they have large surface area per unit volume leading to better interactions between the particles and polymeric matrix thus exhibiting remarkable mechanical properties [63]. The tiny size, large surface area and quantum effect as well as strong interfacial interaction between the organic polymer and inorganic particles all these factors contributed to improve the mechanical properties of the polymers [64]. Asar *et al.* [9] stated that using metal oxide with different particle sizes get the advantage of providing additional advance of some mechanical and physical properties of denture base acrylic by inhibiting the spaces among oxide particles and leading to have further particles per unit volume of polymer. This high polymer density leads to increased hardness even at low filler concentration [65].

Another important consideration playing a major role on the mechanical properties of particulate filled polymer composites is excellent adhesion between reinforcements and polymer matrix [17,18]. Kamonkhantikul., et al [31] investigated the effect of adding the similar weight of silanized and non-silanized ZnO nanoparticles on the antifungal, mechanical and optical characteristics of PMMA. They proved that silanized groups had improved properties. In the present study, the surface of the inorganic filler was modified with organic compound in order to achieve chemical blending or unification of the inorganic filler with the organic matrix of the acrylic resin to enhance denture base properties. This strategy successfully improved surface hardness of the tested heat cured acrylic material. It is clear that acrylic resin samples modified with ZDA have greater hardness than unmodified one. In addition the material became significantly harder as the ZDA percent increased from 5% to 10% in the modified acrylic.

Another reason of the increase of hardness property of the modified acrylic samples with ZDA was thought to be the crosslinking behavior of ZDA. Azevedo *et al.* (46) found that both Lucitone 550 and Duraliner II materials result in more rigid materials than other tested denture polymers due to their high constituent of cross-linking agents. Polymeric materials contain cross-linking agents result in a more rigid polymer structure (66,67). Exchanging the van der Waal's forces between polymer chains by stronger carbon-carbon (C-C) primary bonds reduces the mobility of polymer segments by holding the chains more tightly together (68) thus increasing polymer hardness. Crosslinking restricts the ability of individual polymer chains to slide pass each other and provides insolubility, rigidity, and stiffness to the polymer (65).

Therefore, the null hypothesis assumed that these modifying procedures do not diminish the surface hardness of the heat cured acrylic resin was accepted. Further research is required to investigate the possibility of clinical use of these promising acrylic resins as biomaterials.

CONCLUSIONS

This study is a continuance and extension of a previously published work where the efficiency of new different modifying ways of denture base acrylic resin was demonstrated.

The present study emphasized the improvement of surface hardness of heat cured acrylic resin modified by addition of ZnO in the stated techniques. While taking into consideration all other influences and variables, the good adhesion of fillers with acrylic matrix may have a significant impact in the ability to reach the desired enhancement of acrylic properties.

The results of the current study showed a general increase of the surface hardness of the experimental groups in comparison with the control group. Hardness was significantly enhanced by either adding 10% by weight of thermally activated ZnO or by copolymerizing it with 10% by weight of ZDA to get poly (methyl methacrylate -co-zinc acrylate) copolymer.

Declaration of interest

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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