Evaluation the effect of nano-fillers (TiO_2, AL_2O_3, SiO_2) addition on glass transition temperature, E-Moudulus and coefficient of thermal expansion of acrylic denture base material

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ABSTRACT

Background: The PMMA polymer denture base materials are low in thermal and strength properties. The aim of the study was to investigate the change in glass transition temperature, E-Moudulus and coefficient of thermal expansion of acrylic denture base material by addition of $Al2O_3$, TiO_2 and SiO_2nano-fillers in 5% by weight.

Materials and methods: The type of polymerization is free radical bulk polymerization. one hundred twenty (120) specimens were prepared , the specimens were divided into four groups according to the material had been added (one control and three for $Al2O_3$, TiO_2 and SiO_2nanocomposite) each group was subdivided in to three groups according to the test had been done on it, the degree of transition (Tg) was measured by The differential scanning calorimeter (DSC), E-Modulus and coefficient of thermal expansion and contraction was measured by Thermo Mechanical Analyzer (TMA) .Each sample was tested at different temperatures (30,40,50,60,70C°).

Results: Highly significant decrease in coefficient thermal expansion and contraction and in E-Modulus occurred in acrylic incorporated with $Al2O_3$, TiO_2 and SiO_2 nano-fillers in 5% by weight when compared to control group. For glass transition temperature a significant increase had occurred with the addition of nanofillers at 5% when compared to control group.

Conclusion: The results showed that the polymer nanocomposites possess material properties different from that of unmodified PMMA, nanocomposite has thermal and mechanical stability more than heat neat PMMA.

Keyword: Acrylic denture base, nano fillers, thermal properties. **(J Bagh Coll Dentistry 2014; 26(1):37-41).**

الخلاصة

الخلفية : البوليمر بدلة المواد الأساسية PMMA منخفضة في الخصائص الحرارية والقوة .. وكان الهدف من الدراسة للتحقيق التغيير في درجة حرارة التحول الزجاجي ، E-Moudulus و معامل التمدد الحراري لل مادة الاكريليك قاعدة أسنان بإضافة AL2O3 ، TIO2 و SIO2 نانو الحشو في 5 ٪ من وزنها .

المواد و الأساليب: نوع البلمرة مجانية البلمرة الراديكالية الأكبر . قد أضيفت أعدت مائة وعشرين (120) العينات ، تم تقسيم العينات إلى أربع مجموعات وفقا للمادة (عنصر تحكم واحد وثلاثة ل AL2O3، TIO2 و SIO2 بمركب متناهي في الصغر) تم تقسيم كل مجموعة إلى ثلاث مجموعات وفقا لاختبار زيارتها تم القيام به على ذلك، تم قياس درجة التحول (تيراغرام) بواسطة المسعر المسح التفاضلي (DSC، E- معامل و معامل التمدد الحراري والانكماش و تقاس الحرارية محلل الميكانيكية (TMA) . تم اختبار كل عينة في درجات حرارة مختلفة (30،40،50،60،70 ° C) .

النتائج : انخفاض كبير للغاية في معامل التمدد الحراري والانكماش و E- معامل وقعت في الاكريليك تندمج مع AL2O3، TIO2 و SIO2 نانو الحشو في 5 ٪ من الوزن مقارنة بالمجموعة الضابطة . ل درجة حرارة التحول الزجاجي زيادة كبيرة حدثت مع إضافة المالئة النانومترية في 5 ٪ مقارنة بالمجموعة الضابطة .

الاستنتاج : أظهرت النتائج أن nanocomposites و البوليمر تمتلك خصائص مواد مختلفة عن تلك التي PMMA معدلة ، بمركب متناهي في الصغر لديه الاستقرار الحراري و الميكانيكي أكثر من الحرارة PMMA أنيق.

الكلمة الرئيسية: أكريليك قاعدة أسنان ، والحشو نانو، الخواص الحرارية .

INTRODUCTION

Polymer nanocomposite gained attention of researches because of their novel properties that are derived from the two components [1].The addition of very small amount less than 5%fillers to apolymeric matrix has significant impact on the thermal and mechanical properties of the polymer [2].The PMMA polymer denture base materials are low in thermal and strength properties [3,4]. when The temperature increases polymers show a large variation of mechanical and physical properties .The acrylic resin is hard and glass like at room temperature and with increase in the temperature to a critical temperature a transition occur to flexible and soft material, this transition occurs over a critical temperature termed glass transition temperature (Tg)[5]. At (Tg) temperature a sharp increase in the thermal expansion coefficient occurs, indicating increased molecular mobility [6].

The dimensional stability of acrylic denture base resin was related to this temperature, as the polymers goes from a hard state to a soft state. The coefficient of thermal expansion of the polymer changes, this change corresponds to Tg [7] .The denture should be above the Tg while it is in service during finishing and polishing by dentist and technician and during cleaning in hot water by the patient. Now attention is directed toward addition of inorganic nanoparticles to PMMA to improve its thermal stability and thermal mechanical behavior [8-10].

The nanofillers particles are expected to disperse more homogeneously than large microfillers within a polymer host, this interaction between nanofiller and polymer lead to the properties of the composite materials. Nanocomposites display glass transition temperature and thermal degradation that are higher 15 °C and 60 °C than PMMA respectively [11]. Nanocomposites had higher storage modulus and higher glass transition temperature (Tg) than

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pure PMMA which were measured by dynamic mechanical properties [12]. There is improvement in glass transitiontemperature and in heat resistance of nanocomposite reached to 16 °C and 14 °C respectively [13]. Young modulus decreased by 20% after addition of nanofillers to PMMA nanocomposite. The best result in physical and mechanical properties was observed in denture base reinforced with 5wt% of nano-ZrO_2 [14].

In this study three types of inorganic nanofillers were used that were added to heat cure PMMA at 5wt% and evaluate the effect ofthis addition on physical (Tg, coefficient of thermal expansion and contraction) and mechanical property (E-Modulus) of heat cured acrylic denture base material.

MATERIALS AND METHODS

Table 1: List of the materials that were used

Material	TiO_2nanofiller	Al_2O_3nano filler	SiO_2 nanofiller	Heat-curing resin for denture
Manufacturer	Sigma-Aldrich Germ.	Sigma-Aldrich Germany.	Sigma-Aldrich Germ.	Superacr-yl plus Czechoslovakia

Test specimens preparation

Two different metal patterns were constructed according to the required test. The pattern that was constructed for coefficient of thermal expansion and contraction test and E-Modulus test was a cylindrical shaped specimen (15mm x 6mm) length, diameter respectively [5] .For glass transition temperature test: a bar shaped specimen was constructed (65mm X 10mm X 2.5mm) length, width, thickness respectively [15-17].

Mould preparation

Addition of fillers

An electronic balance was used with accuracy of (0.0001g) (Sartorius BP 30155, Germany) for addition of nanofillers powder at weight 5% to monomer. After the addition of nano filler to monomer, the powder of fillersseparated into individual nano crystals which were dispersed in the monomer byusing sonication apparatus (Soniprep-150, England) at 120 W, 60 KHz for 3 minutes [14].To reduce the possibility of particle aggregation

Proportioning and mixing of the acrylic

The suspension of the monomer with nano filler was immediately mixed with acrylic powder. All materials were mixed and manipulated according to manufacture's instructions for acrylic resin at ratio of (2.5g:1g) P/L .The mixing was carried outby a clean wax knife in a clean and dry mixing vessel and mixed for 30 second. The mixture was then covered and left to stand until a dough stage was reached.Using a conventional denture flasking technique.

Thermal analysis and mechanical tests

1-Measuring of Tg .

a-Specimen form: The specimen should be in powder form 10 mg powder is prepared so the acrylic specimens were shaved with a sharp knife (figure 1) .

Figure 1: Prepared powder form

b-The procedure: The differential scanning calorimeter (DSC-60 from Shimadzu, Japan) (figure 2) is an instrument that is used to determine the thermal transition (Tg). The DSC device is connected to a control and program unit that show the data ,Tg value is determined by computer .The acrylic powder of the specimen was put in an aluminum pan of DSC device, with an empty aluminum pan as a reference, Tg value was determined on DSC thermogram. Before starting measurement the heating rate used was (10 °C/min) and chart speed of (20mm/min) was selected for all the heating operations. Using a predefined temperature range from 20°C to 190 °C in dynamic air atmosphere (flow rate 25 cm^3/min).

Figure 2: DSC device

2-Measuring of the coefficient of the thermal expansion and contraction ( ) .

a-specimen form :The acrylic specimen should be in cylindrical form of dimension 15mm in length and 6 mm diameter to coincide the probe of

thermo-mechanical analyzer(TMA) which is 5 -6 mm in diameter (figure 3).

Figure 3: Cylindrical form.

b-The procedure: Thermo Mechanical Analyzer (TMA, PT1000 from Linseis, UN) (figure4) is an instrument that is used to determine thecoefficient of thermal expansion and contraction (∝).The probe of TMA device has 5-6 mm in diameter which rests on cylindrical specimen of 6mm in diameter and 15 mm in length .TMA device was connected with programs units that show the data on computer . Before measurement a heating rate of 10 C/min was selected [15].

Figure 4: TMA device

Coefficient of thermal expansion and contraction (∝) was determined by measuring the change in length (L) per unit length for each °C temperature change (t)or measuring the change in volume △y increase the temperature at constant pressure per unit volume. In this study the following equation was used:

$$(\propto)=\left(\frac{\triangle(L)mm}{L1\,m\triangle*(t)C}\right)$$

3- Measuring of Modulus of Elasticity (E-Modulus).

a- Specimen form: The acrylic specimen should be in cylindrical form of dimension 15mm in length and 6 mm diameter.

b-The procedure: The same method as in TMA was used,a heating rate of 10 °C/min and load of 50 gm was selected [15]. E-Modulus was determined by computer by measuring the ratio of elastic stress to elastic strain. E=stress/strain

RESULTS

Mean values, standard deviation, standard error, t-test and p-value forglass transiaion temperatureare presented in Table (2).

Table 2: Descriptive of glass transition temperature

	Control	TiO2	SiO2	AL2O3	ANOVA
Mean	85.6	118.6	102.4	113.2	F-test=60.852 P<0.01 HS
SD	6.693	2.607	3.361	2.588	
t-test	-	8.578	4.221	7.819	
P-value	-	0.001	0.013	0.001	
Sig	-	HS	S	HS	

Coefficient of thermal expansion and contraction tests result are presented in Table (3,4,5,6,7),one way ANOVA test betweengroups at different temperatures (30,40,50,60,70C°) is presented in Table(8) .

Table 3: Descriptive data of coefficient of thermal expansion and contraction at 30 C°

Temp. 30 C°	Control	TiO2	SiO2	AL2O3
Mean	72	57	68	63
SD	1.58113	1.5811	1.58113	1.58113
t-test	-	17.928	4.781	10.757
P-value	-	P<0.01	P<0.01	P<0.01
Sig	-	HS	HS	HS

Table 4: Descriptive data of coefficient of thermal at 40 C°.

Temp. 40 C°	Control	TiO2	SiO2	AL2O3
Mean	85	75	81	77
SD	1.5811	1.5811	1.5811	1.5811
t-test	-	7.906	2.902	9.562
P-value	-	0.001	0.044	0.001
Sig	-	HS	S	HS

Table 5: Descriptive data of coefficient of thermal at 50 C°

Temp. 50 C°	Control	TiO2	SiO2	AL2O3
Mean	93	86	90	86
SD	1.58113	2.2360	2.549	2.549
t-test	-	7.376	5.447	12.780
P-value	-	0.002	0.005	P<0.01
Sig	-	HS	HS	HS

Table 6: Descriptive data of coefficient of thermal expansion and contraction at 60 C°

Temp. 60 C°	Control	TiO2	SiO2	AL2O3
Mean	100	95	96	93
SD	1.58113	1.5811	1.58113	1.5811
t-test	-	9.129	2.981	5.916
P-value	-	0.001	0.041	0.004
Sig	-	HS	S	HS

Table 7: Descriptive data of coefficient of thermal expansion and contraction at 70 C°

Temp. 70 C°	Control	TiO2	SiO2	AL2O3
Mean	105	100	97	98
SD	2.5495	2.5495	3.3911	3.1622
t-test	-	0.00	7.628	2.746
P-value	-	1.000	0.002	0.049
Sig	-	NS	HS	S

Table 8: ANOVA of coefficient of thermal expansion and contraction

ANOVA	Control	TiO2	SiO2	AL2O3
F-test	265.8	388.56	143.43	200.31
P-value	P<0.01	P<0.01	P<0.01	P<0.01
Sig	HS	HS	HS	HS

Mean values, standard deviation, standard error, t-test and p-value for E-Modulus tests result are presented in Table (9,10,11,12,13), one way ANOVA test between groups at different temperatures (30,40,50,60,70C°) is presented in Table (13) .

Table 9: Descriptive data of E-Modulus (N/mm^2) at 30 C°

Temp. 30 C°	Control	TiO2	SiO2	AL2O3
Mean	2119	451	1233	1738
SD	17.117	4.1231	26.580	24.738
t-test	-	286.06	63.627	105.657
P-value	-	P<0.01	P<0.01	P<0.01
Sig	-	HS	HS	HS

Table 10: Descriptive data of E-Modulus (N/mm^2) at 40 C°

Temp. 40 C°	Control	TiO2	SiO2	AL2O3
Mean	2522	531.2	1405	2305.4
SD	11.510	22.653	21.908	25.880
t-test	-	215.502	112.54	14.554
P-value	-	P<0.01	P<0.01	P<0.01
Sig	-	HS	HS	HS

Table 11: Descriptive data of E-Modulus (N/mm^2) at 50 C°

Temp. 50 C°	Control	TiO2	SiO2	AL2O3
Mean	2748.8	602.8	1772.6	2684.2
SD	74.30141	23.40299	25.48137	27.09613
t-test	-	48.786	42.05	2.932
P-value	-	P<0.01	P<0.01	0.043
Sig	-	HS	HS	S

Table 12: Descriptive data of E-Modulus (N/mm^2) at 60 C°

Temp. 60 C°	Control	TiO2	SiO2	AL2O3
Mean	2785	682.2	2068.4	2023.4
SD	24.217	25.655	27.790	49.952
t-test	-	131.26	82.167	36.05
P-value	-	P<0.01	P<0.01	P<0.01
Sig	-	HS	HS	HS

Table 13: Descriptive data of E-Modulus (N/mm^2) at 70 C°

Temp. 70 C°	Control	TiO2	SiO2	AL2O3
Mean	2824	772.6	2217	2201.8
SD	97.203	14.518	78.185	129.438
t-test	-	41.27	13.001	6.146
P-value	-	P<0.01	P<0.01	0.004
Sig	-	HS	HS	HS

Table 14: ANOVA of E-Moudulus (N/mm^2)

ANOVA	Control	TiO2	SiO2	AL2O3
F-test	134.52	202.8	505.7	143.9
P-value	P<0.01	P<0.01	P<0.01	P<0.01
Sig	HS	HS	HS	HS

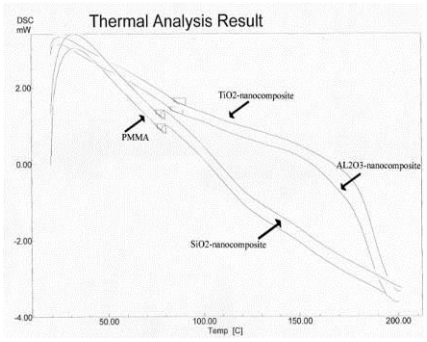

Figure: 5 DSC curve

DISCUSSION

The present study was conducted to evaluate and compare the effect of addition ($Al2O_3$, TiO_2 and SiO_2nano-fillers) to PMMA on thermal and mechanical properties of acrylic denture base. These types of nanofillers were used because of their thermal properties and also because of being white are less likely to alter esthetic. The thermal stability of the samples was examined by TMA

and DSC [16]. Thermal properties and E-modulus are tested over a physiologic temperature range (30-70C°). The introduction of nanofillers into PMMA caused decrease in the value of coefficient of expansion and contraction, statistically highly significant decrease in low temperature at 30 and became significant decrease at high temperatures (60,70C°). The decrease in the thermal expansion coefficient was due to the greater interfacial interaction between nanofillers and matrix which limited the molecular mobility of polymer [12,13]. Homogenous distribution of very fine size and high surface area of nanofiller enable them to restrict the motion of macromolecule chains and enhance thermal properties [6,18], that means the PMMA nanocomposite has thermal stability more than neat PMMA ,in addition to decrease in volume of PMMA with present of nanofillerat 5%.

In this study Tg measured from the temperature of the peak maxima of DSC curves obtained for the pure PMMA and PMMA nanocomposite. The value of glass transition temperature increased for Al_2O_3 and SiO_2nanocomposite at 5wt%, the DSC peak shifted toward higher temperature when compared to control group, it was found that the addition of TiO2 nanofillers to PMMA caused highly increased in Tg , it is shows in figure (5),this may be due to the melting temperature of nanofillers are higher, the magnitude of the shift being dependant onthe type and amount of nanofillers. The addition of nanofillers at 5% to PMMA led to decrease E-Modulus beyond that of pure PMMA, these changes are due to excessive interactions between PMMA and the large surface area of nanofillers

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