

# Mechanical and Thermal Properties of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> Nanoparticles Addition Heat Cured Acrylic Resin

Berrin AKKUŞ<sup>1</sup>, Şakir Yazman<sup>2</sup>, A. Nilgun OZTURK<sup>3</sup>, Ahmet AKDEMİR<sup>4</sup>

<sup>1</sup>Cihanbeyli Technical Collage, Selçuk University, Cihanbeyli, Konya, Turkey

<sup>2</sup>İlgin Technical Collage, Selçuk University, Konya, Turkey

<sup>3</sup>Department of Prosthodontics, Selçuk University, Konya, Turkey

<sup>4</sup>Department of Mechanical Engineering, Selçuk University, Konya, Turkey

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## ABSTRACT

In this study, the effects of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles on hardness, surface roughness, thermal properties and microstructure of heat cured acrylic resin were investigated.

**Materials and Methods:** 1 wt% , 3 wt% Al<sub>2</sub>O<sub>3</sub> and 1 wt% , 3 wt% SiO<sub>2</sub> nanoparticles were added to heat cured acrylic resin. Fifty specimens were divided to five groups (n=10). Group 1. Acrylic resin without nanoparticle (control group), Group 2. Acrylic resin with 1 wt% Al<sub>2</sub>O<sub>3</sub> nanoparticles, Group 3. Acrylic resin with 3 wt% Al<sub>2</sub>O<sub>3</sub> nanoparticles, Group 4. Acrylic resin with 1 wt% SiO<sub>2</sub> nanoparticles, Group 5. Acrylic resin with 3 wt% SiO<sub>2</sub> nanoparticles. Specimens in dimensions of 60 x 12 x 4 mm were prepared according to ISO 1567 standard. Hardness, surface roughness and thermal properties such as curing behaviour, thermal stability were examined. Microstructure was examined by SEM (scanning electron microscopy). Statistical analysis was performed with SSPS17.0 (SPSS Inc., Chicago, USA).

**Results:** Significant increase in hardness of heat cured acrylic resin didn't occur with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles. The highest surface roughness value was observed in heat cured acrylic resin with 1% and 3% Al<sub>2</sub>O<sub>3</sub> nanoparticles.  $T_g$  values of groups with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles were higher than that of control group.  $T_p$  values of groups with Al<sub>2</sub>O<sub>3</sub> nanoparticle was lower than those of groups with SiO<sub>2</sub> nanoparticle.  $\Delta H$  value of control group was higher than other groups.  $\Delta C_p$  value of group with 3% SiO<sub>2</sub> nanoparticle was the highest.

**Conclusion:** The highest surface roughness value was observed in heat cured acrylic resin with 1% and 3% Al<sub>2</sub>O<sub>3</sub> nanoparticles.  $T_g$  values of groups with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles were higher than that of control group.

**Keywords:** Acrylic resin, nanoparticle, hardness, surface roughness, thermal properties, SEM.

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## INTRODUCTION

Poly (methylmethacrylate) (PMMA) is the most commonly used material in construction of denture base since 1930. This material is not ideal in every respect and it is the combination of various rather than one single desirable of properties that accounts for its popularity and usage. Despite its popularity which satisfy aesthetic, simple processing and easy repair, the main problems associated with PMMA as denture base material are poor strength particularly under fatigue failure inside the mouth, impact failure outside the mouth and lack of radio-opacity<sup>[1]</sup>. Recently, much attention has been directed toward the incorporation inorganic nanoparticles into PMMA to improve its properties. The properties of polymer nanocomposites depend on the type of incorporating nanoparticles, their size and shape, as well as the concentration and interaction with the polymer matrix<sup>[2]</sup>.

Nanoparticles have been increasingly used in material science for its wear and tear resistance and anti-corrosion abilities. The principle behind the usage of nanoparticles is that alteration of filler size is considered responsible for the performance of the material (PMMA) in aspects of both polishability and fracture resistance<sup>[3]</sup>. Surface roughness is an important property of acrylic resin since denture bases are in contact with buccal tissues, and a rough surface may affect tissues health due to microorganism accumulation<sup>[4]</sup>.

Hardness is an important physical property of acrylic resins, which makes these materials to resist plastic deformation, measuring usually by penetration, and to be used for manufacturing denture bases that withstand forces, such as originating from occlusion and mechanical denture cleansing, increasing the long term clinical use of the dental prosthesis [5].

Thermal analysis is defined as a group of techniques in which a physical property of a polymer is observed under a controlled temperature program. The changes in the properties of the sample during the heating process can be monitored using this analysis. Measurements are generally repeated, and the rate of heating is often linear over time. These measurements are shown thermal analysis curves, and thermal events in the sample are related to the trends of these curves. Differential scanning calorimetry (DSC) and thermogravimetry (TGA) are two well-known analytical methods for evaluating the thermal characteristics of polymers [6].

Different type and concentration nanoparticles had been added to acrylic resin to investigate the effect of nanoparticles on mechanical and thermal properties of acrylic resin. Glass transition temperature of acrylic resin increased by adding 5%SiO<sub>2</sub> and 5%Al<sub>2</sub>O<sub>3</sub> and highly increased by adding 5%TiO<sub>2</sub>nanoparticles [7]. Significant increase was observed for hardness of 2.5 and 5% Al<sub>2</sub>O<sub>3</sub> nanoparticles addition specimens. Slight increase was observed for surface roughness of all specimens [8]. Non-significant increase was observed with 1wt%, significant increase was observed with 2wt% and highly significant increase was observed in hardness value of acrylic resin with 3wt% Al<sub>2</sub>O<sub>3</sub> nanoparticles. Surface roughness of acrylic resin didn't change significantly for 1, 2 and 3wt% Al<sub>2</sub>O<sub>3</sub>nanoparticles [9]. In this study, the effects of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles on hardness, surface roughness, thermal properties and microstructure of heat cured acrylic resin were investigated.

### MATERIALS AND METHODS

In this study, hardness, surface roughness and thermal properties of heat cured acrylic resins addition 1 % , 3 wt% Al<sub>2</sub>O<sub>3</sub> and 1 % , 3 wt% SiO<sub>2</sub> nanoparticles were investigated. Fifty specimens were divided to five groups (n=10). Group 1. Acrylic resin without nanoparticle (control group), Group 2. Acrylic resin addition 1wt% Al<sub>2</sub>O<sub>3</sub> nanoparticle, Group 3. Acrylic resin addition 3 wt% Al<sub>2</sub>O<sub>3</sub> nanoparticle, Group 4. Acrylic resin addition 1 wt% SiO<sub>2</sub> nanoparticle, Group 5. Acrylic resin addition 3 wt% SiO<sub>2</sub> nanoparticle. The dimensions of specimens were 60 x 12 x 4 mm according to ISO 1567 standard. The properties of materials were shown in Table 1.

**Table (1): The materials and manufacturers**

Material	Manufacturer
Acrylic resin Polymethyl methacrylate (PMMA)	Meliodent
Al <sub>2</sub> O <sub>3</sub> nano powder ( 99.5% pure, powder size 40-50 nm)	Heraeus Kulzer, Germany
SiO <sub>2</sub> nano powder coated with silane coupling agent (99.5% pure, powder size 15 nm)	MKNANO, Canada

1 % , 3 wt % Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles were mixed with heat cured acrylic resin using mechanic mixture for 30 min. Fifty wax specimens were composed. The dimensions of wax specimens were 60x12x4 mm. Specimens were invested with dental plaster. Flasks were placed to dewax in conventional water bath. They were opened and cleaned to remove traces of wax. Specimens were prepared by hand mixing 2.2 g of PMMA powder with 1.1 mL of methyl methacrylate monomer using a powder to monomer ratio of 2:1 Hydraulic pressure was maintained for 5 minutes before placing the assembly in to boiling water. The conventionally molded, heat cured acrylic resin was placed under compression in 100 °C water for 30 minutes. The specimens were removed from the flasks after curing. All the specimens were grounded with 400 grit size silicon carbide paper. Before test procedure the storage of specimens indistilled water at 37 °C for 48 hours was carried out .

#### HARDNESS TEST

Surface hardness measurements were made for all samples with a digital Rockwell hardness tester. Rockwell hardness tests consist of forcing an indenter (Ball) into the surface of a test piece with two loads. A 1/2 inch diameter ball indenter and with a load of 60 kg force was used for testing.

#### SURFACE ROUGHNESS TEST

To measure the average surface roughness (Ra) of the specimens, a surface roughness tester (SJ-400; Mitutoyo, Kawasaki-Shi, Japan) was used with a 0.01-mm resolution calibrated to a specimen a length of 0.8 mm, 2.4 mm percussion of measure 0.5 mm/s. Three measurements were made for each specimen and the mean value was calculated.

**THERMAL TESTS**

The curing behavior of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles addition heat cured acrylic resin was measured by differential scanning calorimetry (DSC) (METTLER/TOLEDO DSC 1STAR System ) at a heating rate of 10 °C/min from 30 to 300 °C under a nitrogen flow of 30 ml/min.

The thermal stability of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles addition heat cured acrylic resin was analyzed by thermogravimetry analysis (TGA) (METTLER/TOLEDO TGA/DSC 2 STAR System) at heating rate of 10 °C/min from 30 °C to 800 °C under nitrogen atmosphere.

**SEM ANALYSIS**

Using a randomized method, one sample from each group was coated with gold for imaging by scanning electron microscopy (SEM) (Stereoscan S-360, Cambridge, UK). The distributions of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles in acylic resin examined.

**STATISTICAL ANALYSIS**

Statistical analysis was performed with Kolmogorov-Smirnov test of normal distribution and one-way ANOVA followed by Tukey's honestly significant difference (HSD) test with a general linear model procedure in SSPS17.0 (SPSS Inc., Chicago, USA). One-way ANOVA followed by Tukey's HSD test was used with in each acrylic resin group to compare effectiveness of different reinforcements. A significance level of 0.05 was used for statistical tests.

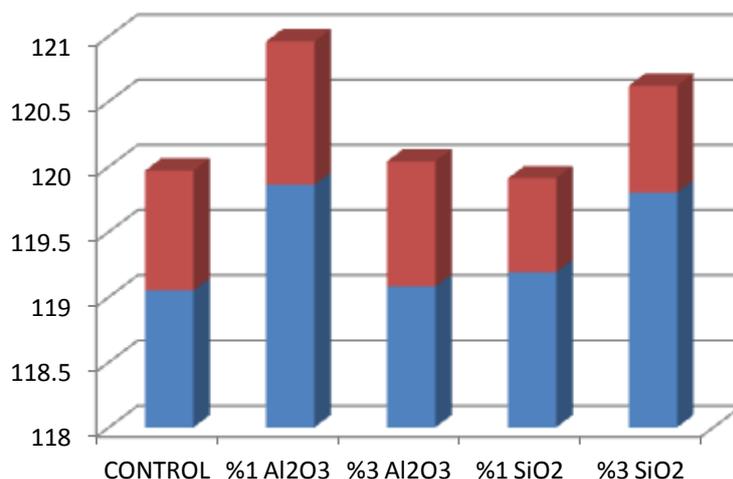
**RESULTS AND DISCUSSIONS**

**HARDNESS TEST**

According to hardness test results significant increase in hardness values of acrylic resin didn't occurred by adding Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticle (p>0.05) (Table 2, Figure 1).

**Table (2): Results of hardness test**

Groups	Mean	SD	Tukey HSD
Control (without nanoparticle)	119,05	0,92	a
Group with 1 % Al <sub>2</sub> O <sub>3</sub>	119,86	1,1	a
Group with 3 % Al <sub>2</sub> O <sub>3</sub>	119,08	0,96	a
Group with 1 % SiO <sub>2</sub>	119,19	0,72	a
Group with 3 % SiO <sub>2</sub>	119,8	0,82	a



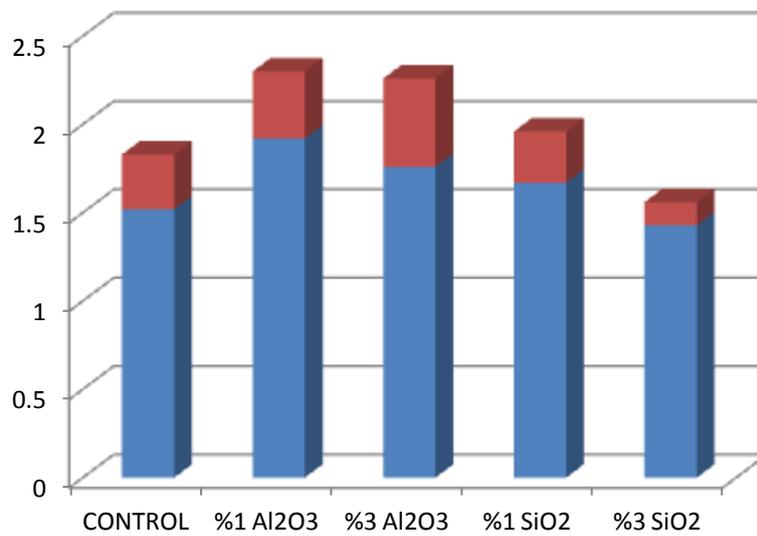
**Fig 1:Results of hardness test**

### SURFACE ROUGHNESS TEST

The highest mean surface roughness value appeared in 1 % and 3 wt%  $Al_2O_3$  ( $p < 0.05$ ) and no significance difference was found in the other groups ( $p > 0.05$ ) (Table 3, Figure 2).

**Table (3): Results of surface roughness test**

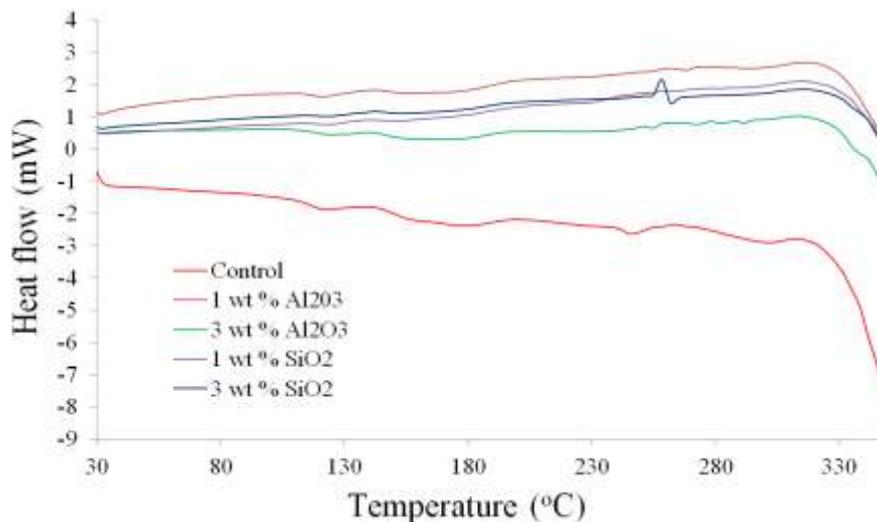
Groups	Mean	SD	Tukey HSD
Control (without nanoparticle)	1,52	0,31	a
Group with 1 % $Al_2O_3$	1,92	0,38	b
Group with 3 % $Al_2O_3$	1,76	0,5	b
Group with 1 % $SiO_2$	1,67	0,29	a
Group with 3 % $SiO_2$	1,43	0,13	a



**Figure 2: Results of surface roughness test**

### CURING BEHAVIOUR

The effect of  $Al_2O_3$  and  $SiO_2$  nanoparticles on curing behaviour of acrylic resin was examined by differential scanning calorimetry (DSC) and dynamic DSC thermograms shown in Fig. 3.



**Figure 3: DSC thermogram**

The glass transition temperature ( $T_g$ ), peak maximum temperature ( $T_p$ ), reaction enthalpy ( $\Delta H$ ) and heat capacity ( $\Delta C_p$ ) were calculated from the thermograms and the results were given in Table 4.

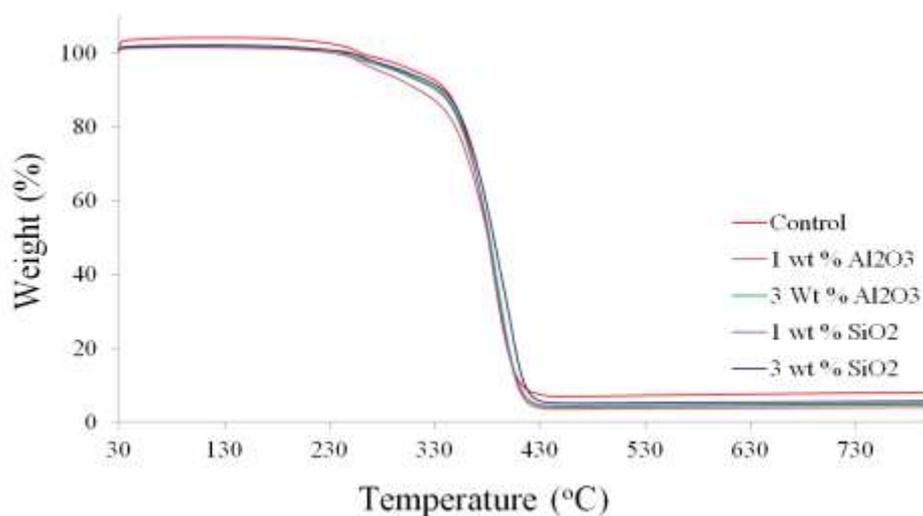
**Table 4. Glass transition temperature ( $T_g$ ), peak maximum temperature ( $T_p$ ), reaction enthalpy ( $\Delta H$ ) and heat capacity ( $\Delta C_p$ ) of groups**

Groups	$T_g$ (°C)	$T_p$ (°C)	$\Delta H$ (j/g)	$\Delta C_p$ (j/g <sup>2</sup> K)
Control (without nanoparticle)	110.77	124.81	313.6	0.182
Group with 1% Al <sub>2</sub> O <sub>3</sub>	111.72	121.57	285.8	1.82
Group with 3% Al <sub>2</sub> O <sub>3</sub>	112.86	119.89	266.5	2.44
Group with 1% SiO <sub>2</sub>	113.63	124.22	302.7	1.92
Group with 3% SiO <sub>2</sub>	115.19	123.36	298.6	3.99

$T_g$  values of groups with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles were higher than that of control group. While  $T_p$  of control group was 124.81 °C, that group with 1% Al<sub>2</sub>O<sub>3</sub> was 121.57 °C and that of group with 1% SiO<sub>2</sub> was 124.22 °C.  $T_p$  values of groups with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles decreased with increasing weight%. These results suggested that Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles had a catalytic effect on curing reactions of acrylic resin.  $T_p$  values of groups with Al<sub>2</sub>O<sub>3</sub> nanoparticle was lower than those of groups with SiO<sub>2</sub> nanoparticle under similar conditions, which due to acceleration of reaction by traces of hydroxyl groups in Al<sub>2</sub>O<sub>3</sub> nanoparticle surfaces.  $\Delta H$  value of control group was higher than other groups.  $\Delta H$  values of groups with Al<sub>2</sub>O<sub>3</sub> nanoparticle was lower than those of groups with SiO<sub>2</sub> nanoparticle. This means that Al<sub>2</sub>O<sub>3</sub> nanoparticles in acrylic network structure absorbed heat and acted as a heat sink in the composites.  $\Delta C_p$  value of acrylic resin increased with adding Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticle.  $\Delta C_p$  value of group with 3% SiO<sub>2</sub> nanoparticle was the highest.

### THERMAL STABILITY

The thermal stability of acrylic resins with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles was measured by thermogravimetry (TGA) at a heating rate of 10 °C/min under a nitrogen atmosphere. The results were shown in Fig. 4. and Table 5.



**Figure 4: TGA thermogram**

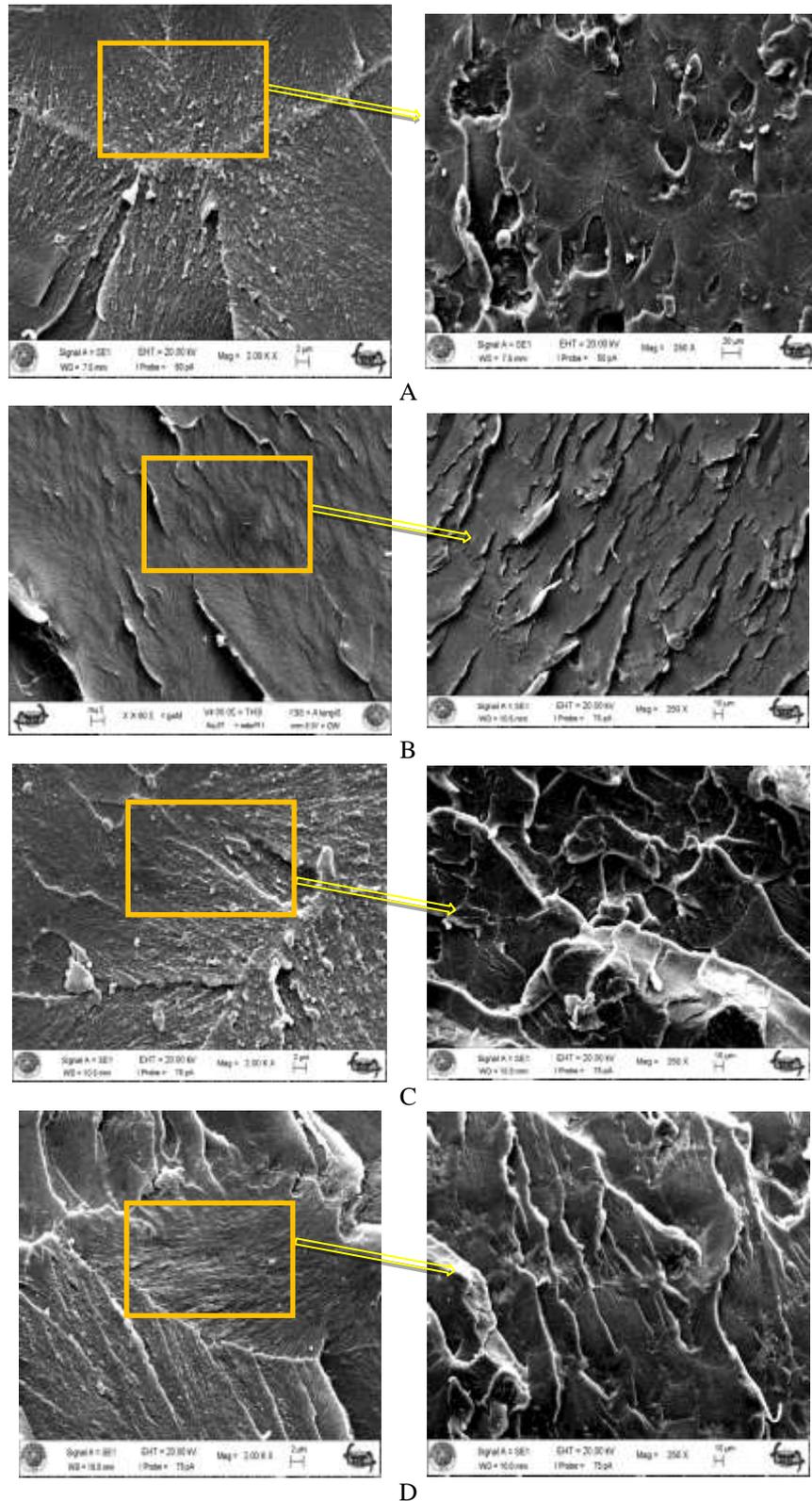
**Table 5. Thermal stability of groups obtained from TGA thermograms**

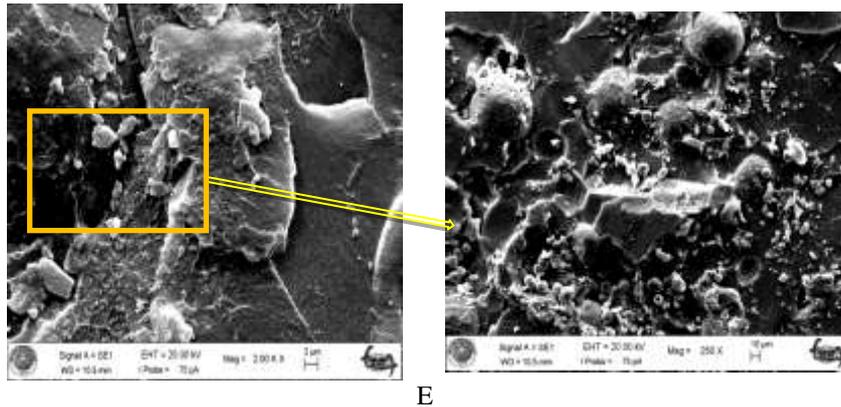
Groups	$T_{5\%}$ (°C)	Char (%) at 800 °C
Control (without nanoparticle)	381.87	7.079
Group with 1% Al <sub>2</sub> O <sub>3</sub>	380.17	3.624
Group with 3% Al <sub>2</sub> O <sub>3</sub>	379.97	4.186
Group with 1% SiO <sub>2</sub>	378.63	4.581
Group with 3% SiO <sub>2</sub>	383.19	5.193

The thermal stability factors including the initial decomposition temperature (the temperature of 5% weight loss,  $T_{d5}$ ) and char at 800 °C, were determined from TGA thermograms. The  $T_{d5}$  values of groups with  $Al_2O_3$  and  $SiO_2$  nanoparticles were similar to that of the control group. The char at 800 °C of control group was higher than other groups. The char at 800 °C of groups with  $Al_2O_3$  and  $SiO_2$  nanoparticles increased with increasing weight%. This suggested that addition of  $Al_2O_3$  and  $SiO_2$  nanoparticles had little effect on thermal stability of acrylic resin.

### SEM ANALYSIS

SEM images of groups were shown in Fig. 5.





**Fig 5: SEM images of groups A: Contol group, B: Group with 1% Al<sub>2</sub>O<sub>3</sub>, C: Group with 3% Al<sub>2</sub>O<sub>3</sub>, D: Group with 1% SiO<sub>2</sub> E:Group with 3% SiO<sub>2</sub>**

It was seen from images that nanoparticle distribution in groups with 1% Al<sub>2</sub>O<sub>3</sub> and 1% SiO<sub>2</sub> was better than others. As nanoparticle weight% increased the effect of crack increased. Many studies were performed on mechanical and thermal properties of acrylic resins addition different nanoparticles. Gfahari et al. 2014 added 0.2 wt% and 2 wt% silver nanoparticles to acrylic resin. It was observed silver nanoparticles increased thermal conductivity of acrylic resin. Safarabadi et al. 2014 investigated the effect of Al<sub>2</sub>O<sub>3</sub> and HA nanoparticles on flexural strength, impact strength, surface hardness and shrinkage behavior of PMMA/HA/Al<sub>2</sub>O<sub>3</sub> hybrid nanocomposites.

Vojdani et al. 2012 added 0.5, 1, 2.5 and 5% Al<sub>2</sub>O<sub>3</sub> nanoparticles to heat polymerized acrylic resin. They determined values of flexural strength, surface hardness and surface roughness. Hardness values increased for all specimens. Significiant increase was observed for 2.5 and 5% Al<sub>2</sub>O<sub>3</sub> nanoparticles addition specimens. Slight increase was observed for surface roughness of all specimens. Jasim and Ismail 2014 added 1, 2 and 3% Al<sub>2</sub>O<sub>3</sub> nanoparticles to heat cured acrylic resin. Transverse strength, thermal conductivity, thermal diffusivity, surface roughness, water sorption and solubility, indentation hardness were determined. According to test results the mean hardness value of control group was 85.4 while that of 3% Al<sub>2</sub>O<sub>3</sub> nanoparticles addition group was 87.3. The mean surface roughness value of control group was 1.2288 while that of 3% Al<sub>2</sub>O<sub>3</sub> nanoparticles addition group was 1.2290. Safi 2014 investigated the effects of 5% TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles on E modulus, glass transition temperature, coefficient of thermal expansion and contraction of acrylic resin. Glass transition temperature of acrylic resin increased by adding 5% SiO<sub>2</sub> and 5% Al<sub>2</sub>O<sub>3</sub> and highly increased by adding 5% TiO<sub>2</sub> nanoparticles.

## CONCLUSIONS

The influences of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles on hardness, surface roughness, thermal properties and microstructure of heat cured acrylic resin were investigated in this study. According to test results the following conclusions found:

1. Significiant increase in hardness of heat cured acrylic resin didn't occured with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles.
2. The highest surface roughness value was observed in heat cured acrylic resin with 1% and 3% Al<sub>2</sub>O<sub>3</sub> nanoparticles.
3.  $T_g$  values of groups with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> nanoparticles were higher than that of control group.
4.  $T_p$  values of groups with Al<sub>2</sub>O<sub>3</sub> nanoparticle was lower than those of groups with SiO<sub>2</sub> nanoparticle.
5.  $\Delta H$  value of control group was higher that other groups.
6.  $\Delta C_p$  value of group with 3% SiO<sub>2</sub> nanoparticle was the higgest.
7. According to SEM analysis nanoparticle distribution in groups with 1% Al<sub>2</sub>O<sub>3</sub> and 1% SiO<sub>2</sub> was better than others.

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