The Effect of Adding (CaO: ZrO2: TiO2) (CZT) NPs Powder on the Thermal Properties and Thermal Expansion of (PMMA) in Bio-Compatible Applications

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Abstract

In this work, a biocompatible polymer was improved with the body of the organism Poly (Methyl Methacrylate) (PMMA) supported by with a three-phase nano bio-ceramic powder (CZT) NPs consisting of a mixture of, oxide zirconium (ZrO2), oxide calcium (CaO) and oxide titanium (TiO2). Samples were acquired using the fluid mixing method and using ultrasound technology to disperse the powder and spread it inside the (PMMA). Nano bio-ceramic powder was added in weight proportions (2%, 4%, 6%, 8%) as a reinforcement to the polymer (PMMA) to prepare nanocomposites. X - ray diffraction (XRD) and electron microscopy (SEM) revealed that (CZT) NPs are uniformly distributed in the PMMA matrix. The technique of thermo mechanical analysis (TMA) was used to diagnose thermal properties and thermal expansion at a specific temperature ranging between (20-200)°C. The outcomes showed a noticeable enhancement for the prepared nanocomposites (PMMA / (CZT) NPs) in the thermal expansion coefficient at temperatures ranging between (30-60)°C for the prepared nanocomposites, compared with non-reinforced polymer samples. Keywords: Nano composites, Poly (Methyl Methacrylate) PMMA, Bio-ceramic and Thermal expansion coefficiten.

Key Words: Poly (Methyl Methacrylate) (PMMA), X - ray Diffraction (XRD), Composite Materials.

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Introduction

In recent years, researches have been done on polymer and ceramic compounds in various applications. Composite materials including ceramic fillings and a polymer matrix have received wide attention from researchers. Significant improvement in mechanical and thermal properties was achieved by inserting fillers into the elastomeric polymer matrices [1,2].

Poly (methyl methacrylate) (PMMA) is a very important thermoplastic material. It is characterized by thermal instability. this advantage placed severe restrictions on its use. To address thermal instability, sundry methods can be used, as the incorporation of nanoparticles into the polymer matrix [3]. It is necessary to understand the thermal behavior of polymer and ceramic compounds, which depends not only on the type and structure of the polymer, but also about the type of filling, the bonding between the polymer and ceramic interface, the thermal characteristic and thermal capabilities of the individual components of ceramics.

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These improved results are obtained by the precise dispersion of selected nanoparticles in the polymer matrix [4,5]. The principle of thermo mechanical analysis (TMA), easily and rapidly measures sample displacement (growth, shrinkage, movement, etc.) as a function of temperature, time, and applied force.

TMA is used to characterize linear expansion, glass transitions, and softening points of materials by applying a constant force to a specimen while varying temperature. To expansion measurement, a probe rests on a sample on a stage with minimal downward pressure.

Other constant force experiments include measurement of penetration, bending, tension, shrinkage, swelling, and creep (sample motion measured as a function of time under an applied load). TMA instrumentation typically spansa temperature range from (-150 to 1000)ºC with controlled cooling from (400to -60)ºC, which is perfect for thermal cycling experiments.

Programmed heating rates of (0.01 to 200)ºC/min are possible. The linear thermal expansion coefficient (α)(K-1) using the equation [6,7]:

$$\alpha = \frac{\Delta l}{l_i \Delta T} \quad (1)$$

$$\Delta l = l_f - l_i \quad (2)$$

$$\Delta T = T_f - T_i \quad (3)$$

$$l_f - l_i / l_i = \alpha \left(T_f - T_i\right) \quad (4)$$

where l_i is the initial length at temperature initial T_i, l_f is the final length at temperature final T_f, α is the linear coefficient of thermal expansion .

The aim of this study is to study the effect of bio-ceramic materials added to Poly (methyl methacrylate) (PMMA) on the thermal properties of Composite and the coefficient of thermal expansion by study their structural, thermal and using various analytical techniques such X -Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Thermo Mechanical Analysis (TMA).

Experimental

Materials and Synthesis of (CZT) NPs, Powders

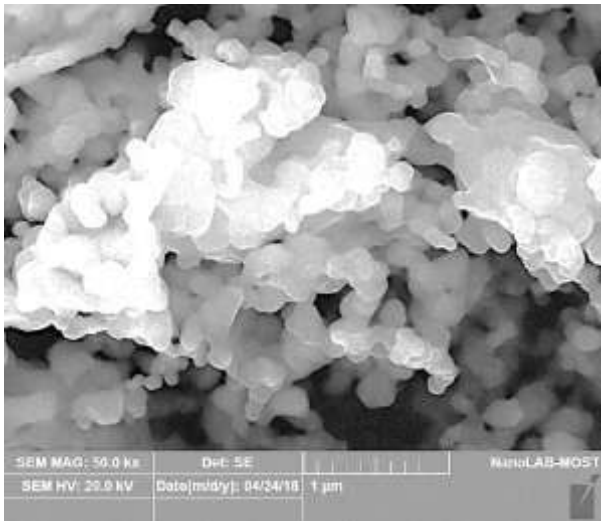
Raw materials for preparing optimized compounds, biocompatible molecules (CZT) NPs,TiO_2 particles, nanoparticle size: 25nm Purity: 99.8%, Chengtou-Stabilized Zaxonium Oxide Nanoparticles/Nano powder (ZrO_2-3Y-99.8% nm) (USA) and calcium oxide CaO Nanoparticles (Laboratory preparation), in order to obtain an interactive form of CaO, in vitro, from eggshells after creasing and crushing to semi-powders and then burning it into the reaction furnace at (450, 700, 900)°C obtained on the $CaCO_3$, powder and was decomposition in an electrical furnace at 1200°C for (3 hours) for synthesizing (CZT) NPs ceramic powder was prepared using the manual fluid mixing up method as well as the ultrasound technique to well distribute ceramic powder, a mixture of nanomaterial (CaO, TiO_2, ZrO_2).

In the current work, (PMMA) is selected as a base material. Poly (methyl methacrylate) (PMMA) Denture base polymer for dental prosthesis a trademark (Spofa Dental a.s., Markova 237,506 01 Jičín, Made in Czech Republic). The powder contains pre-polymerized polymer beads, a radio pacifier and an initiator. The liquid phase consists mainly of the methyl methacrylate monomer and the activator.

Preparation: mixed in the volumetric ratio (3:1) (3 parts of powder, 1 part of liquid) [8,9]. weight fraction, This is done by pour consecutively the powder into the liquid. Composites was prepared using the manual fluid mixing up method as well as the ultrasound technique to well spread (CZT) NPs powder, a hodgepodge of nanomaterial (CaO, TiO_2, ZrO_2). In the composites Biocompatible (PMMA / (CZT) NPs), PMMA was improved with the nanoparticle powder of (CZT) NPs in the weight ratio of (0%, 2%, 4%, 6%, 8%).

The samples did prepare in a cylindrical shape, with a dimension of (30mm) in length and (5 mm) in diameter according to the required measurements, to conduct tests on them aThermo Mechanical Analysis (TMA, PT1000 by Linseis, UN) was used to determine the thermal expansion efficiency (α).

The TMA device is connected to software modules that display data on a computer. Before measurement, a heating rate of (10 °C/min) (15) was chosen. The image of the Scanning Electron Microscope(SEM) shows the particle size of the composites material with magnification limits (50k) as shown in figure(1).



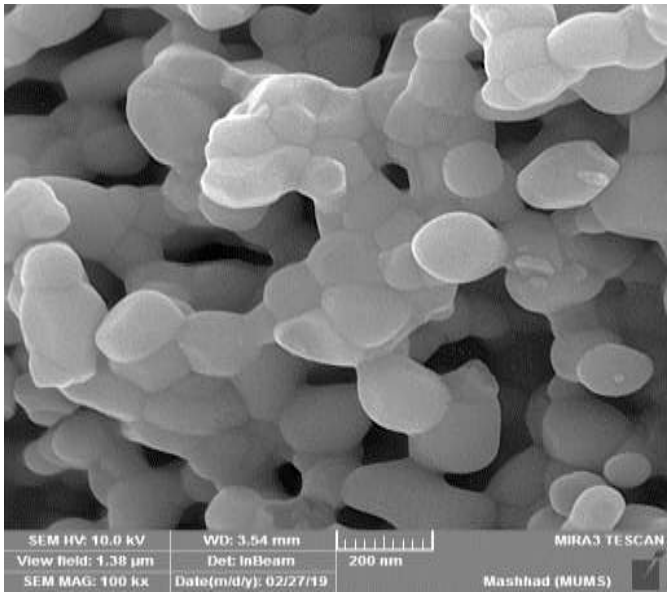


Fig. 1. Scanning Electron Microscope (SEM) for the Composite (CZT) NPs

To determine the percentage of reaction materials, the atomic dispersion spectroscopy (EDS) was used in terms of the energy density shown in figure (2). Figure (3) show X- ray test of (CZT)NPs.

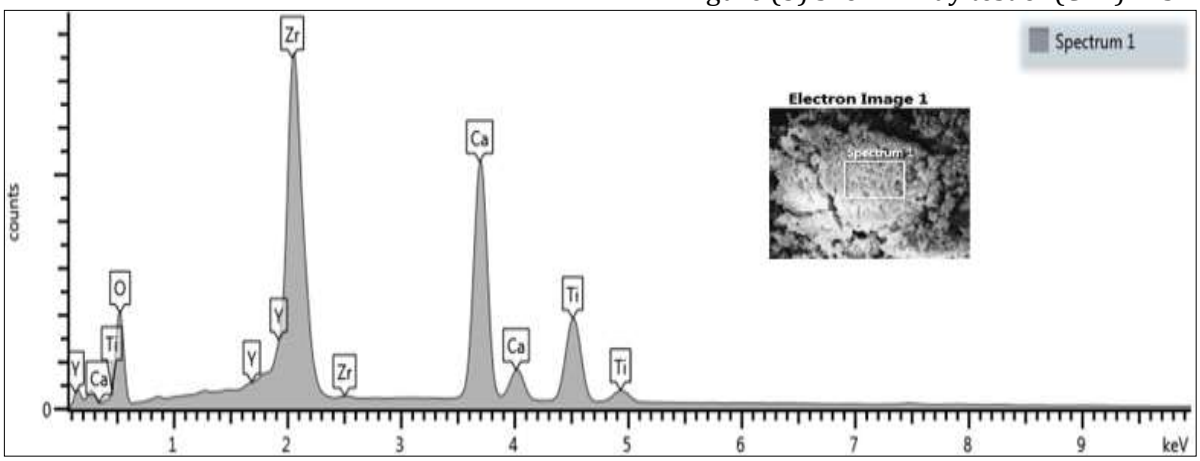


Fig. 2. Energy Dispersive X-ray Spectroscopy (EDX) Spectrum Analysis of (CZT) NPs

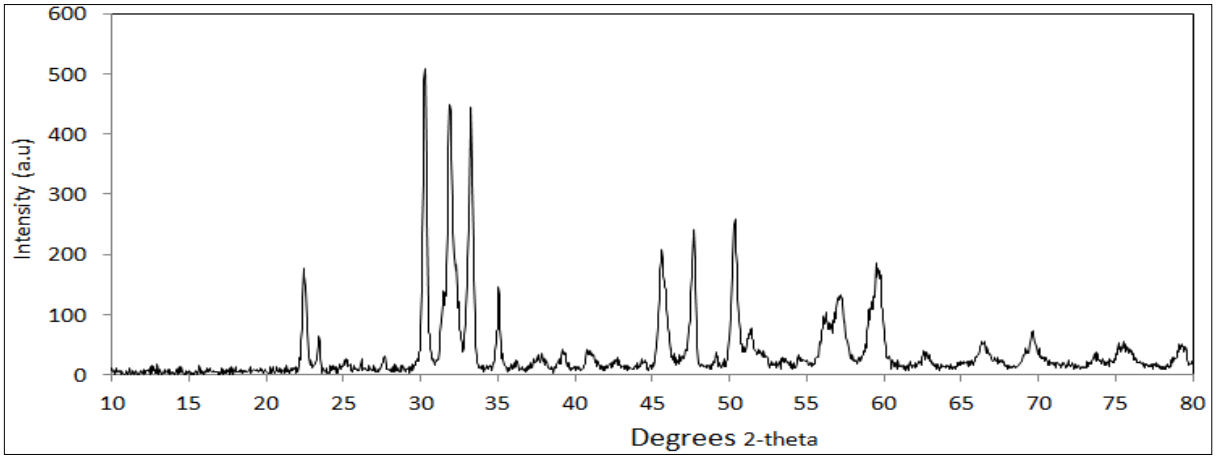


Fig. 3. X- ray Patterns of Bio-ceramic Powder (CZT) NPs

Results and Discussion

Results were obtained from a Thermo Mechanical Analysis test (TMA)as shown in Table (1), and the linear thermal expansion coefficient(α) was calculated according to equation (1) results of the samples tests revealed the change in the linear thermal expansion coefficient (α) with the change in temperature,(20°C-200°C) . Figure (4) show the linear thermal expansion coefficient (α) curves with temperature change and shows the curves behavior for all samples. The samples begin with a small expansion at 20°C, all samples begin withthespeedy expansion at temperatures higher than (40°C) but with different thermal expansion for any sample. Also, figure (5) show the improvement in the thermal expansion (α) of all curves of the spectrum confined to temperatures from (20 to 100)°C for all the percentages (2%, 4%, 6%, 8%) (CZT) NPs compared to the non-reinforced base material (PMMA)and here should focus on a 6% curve at a temperature of 60°C and 40°C as it is considered very appropriate to be one of the applications of bone and dental compensation. The high stability and high resistance of Nano Ceramic materials (CZT) NPs that support the thermal expansion process due to high crystalline structure and its high thermal resistance, and it seems obvious that the peak of the curve at ratio (6 wt.% (CZT) NPs + 94 wt.% PMMA) lowest peak due to density, good Stacking and uniform distribution of ceramic powder and therefore considered as the best ratio and can be adopted in practical application and figure (6) shows diagrams and curves of changes in thermo-mechanical properties with temperature and this corresponds with [10].

Table 1. Experimental TMA results for Thermal Expansion for (PMMA / (CZT) NPs)

Temperature	Thermal Expansion α AKt { E-6 / K }				
	α: 0%	α: 2%	α: 4%	α: 6%	α: 8%
20 ° C	21.91	2.43	13.6	4.1	13.95
40 ° C	73.93	57.07	50.32	39.8	71.23
60 ° C	105.6	84.83	70.44	59.4	72.24
80 ° C	105	53.04	72.4	51.8	52.13
100 ° C	70.43	12.44	64.14	24.7	36.49

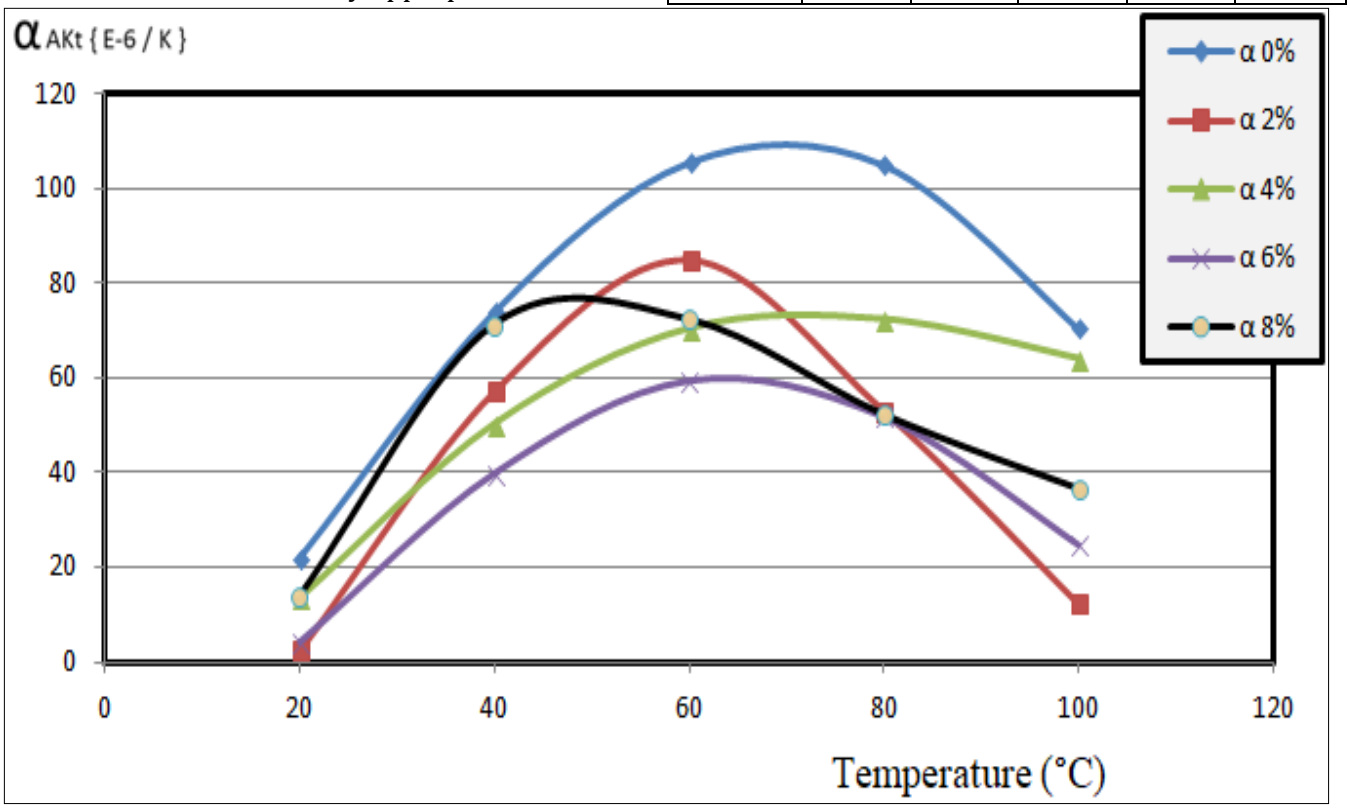


Fig. 4. Linear Thermal Expansion Coefficient with Temperature

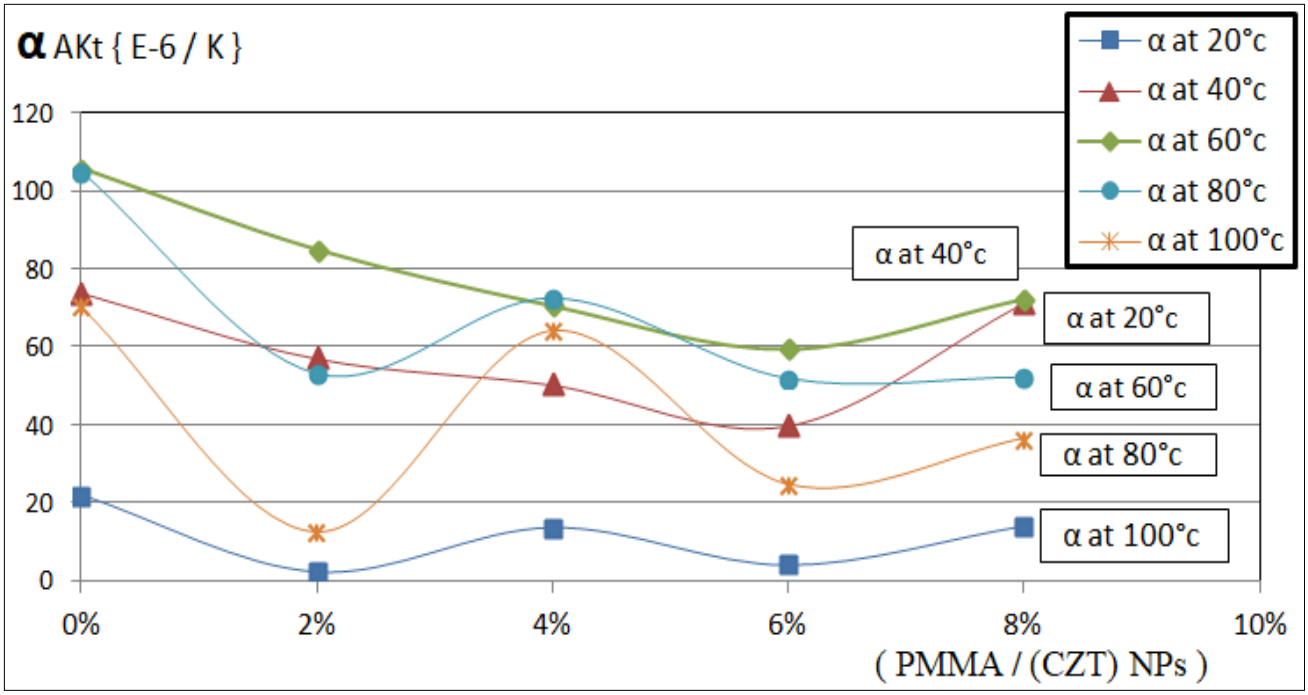
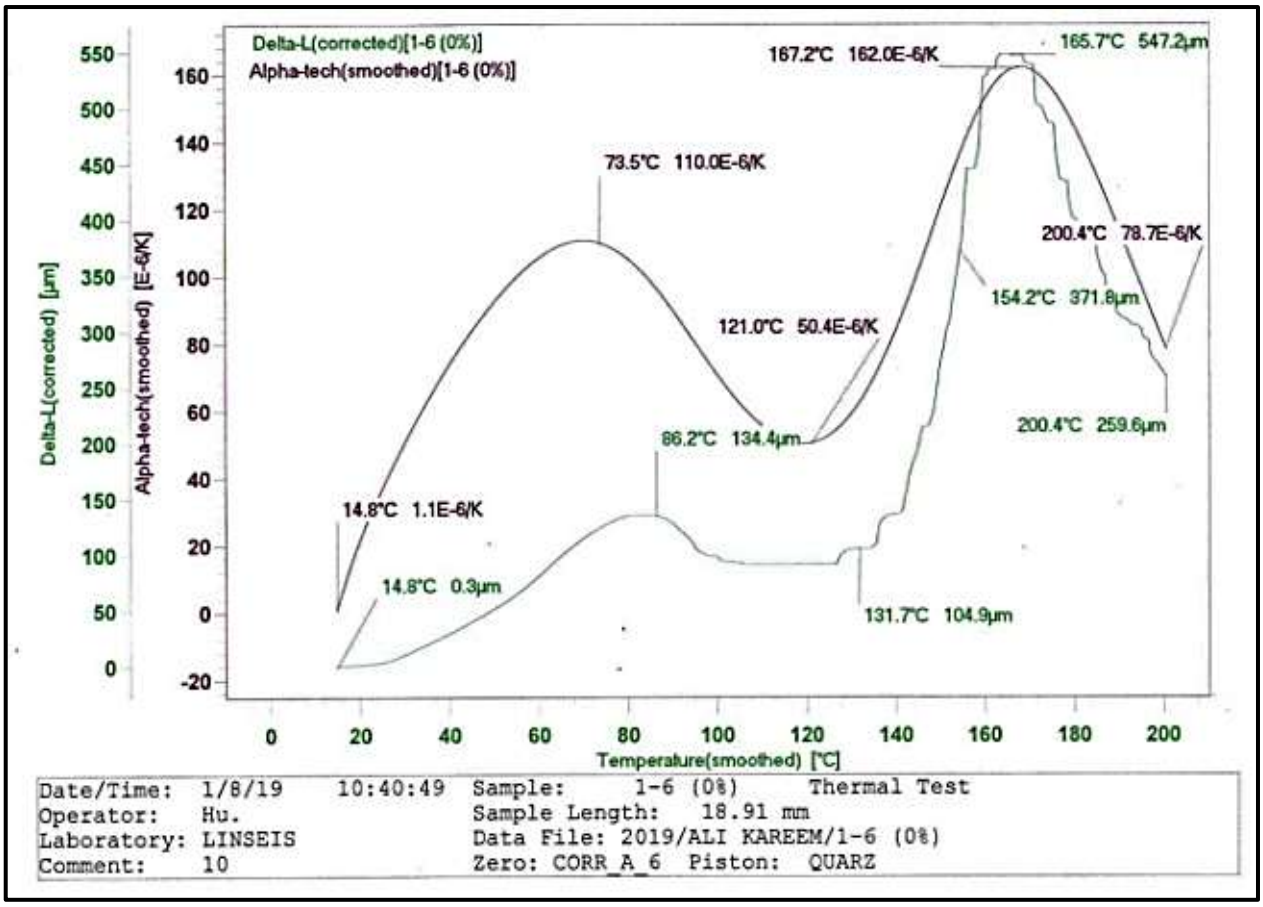
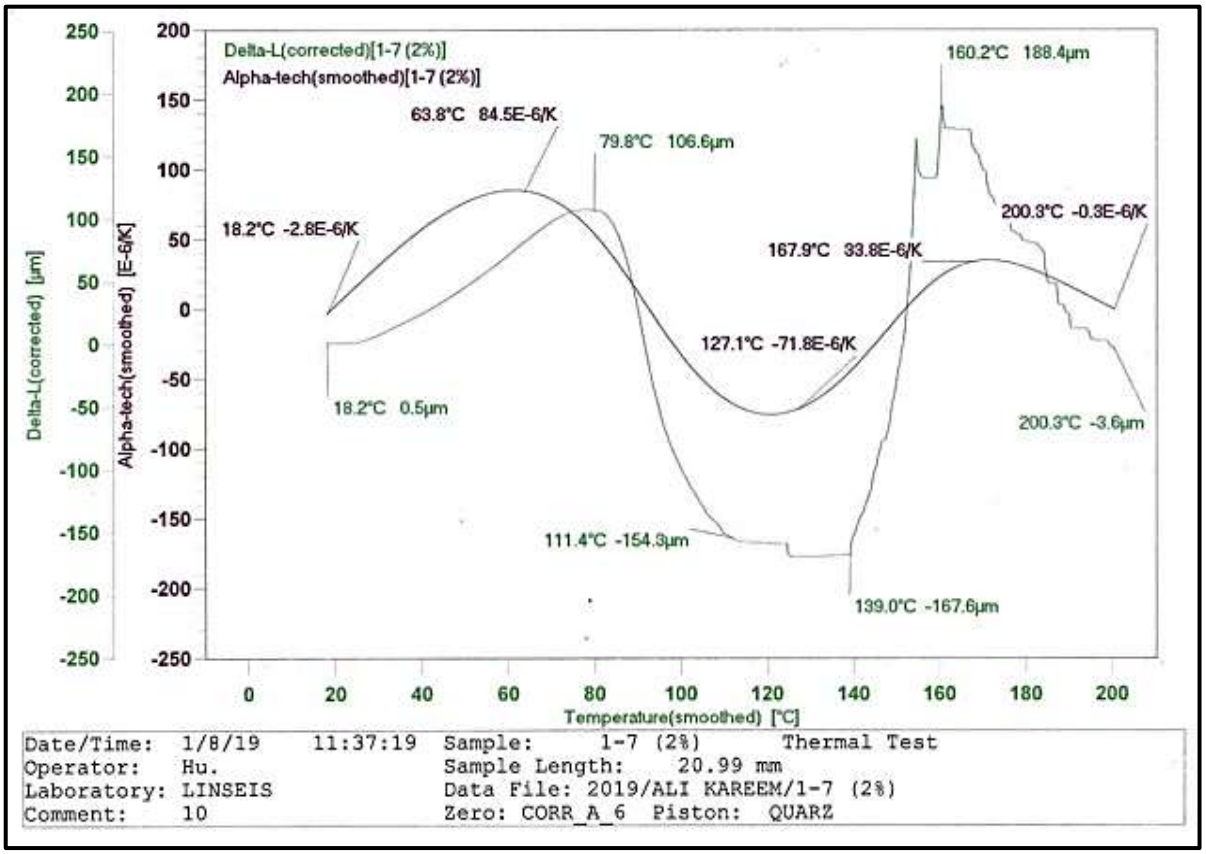
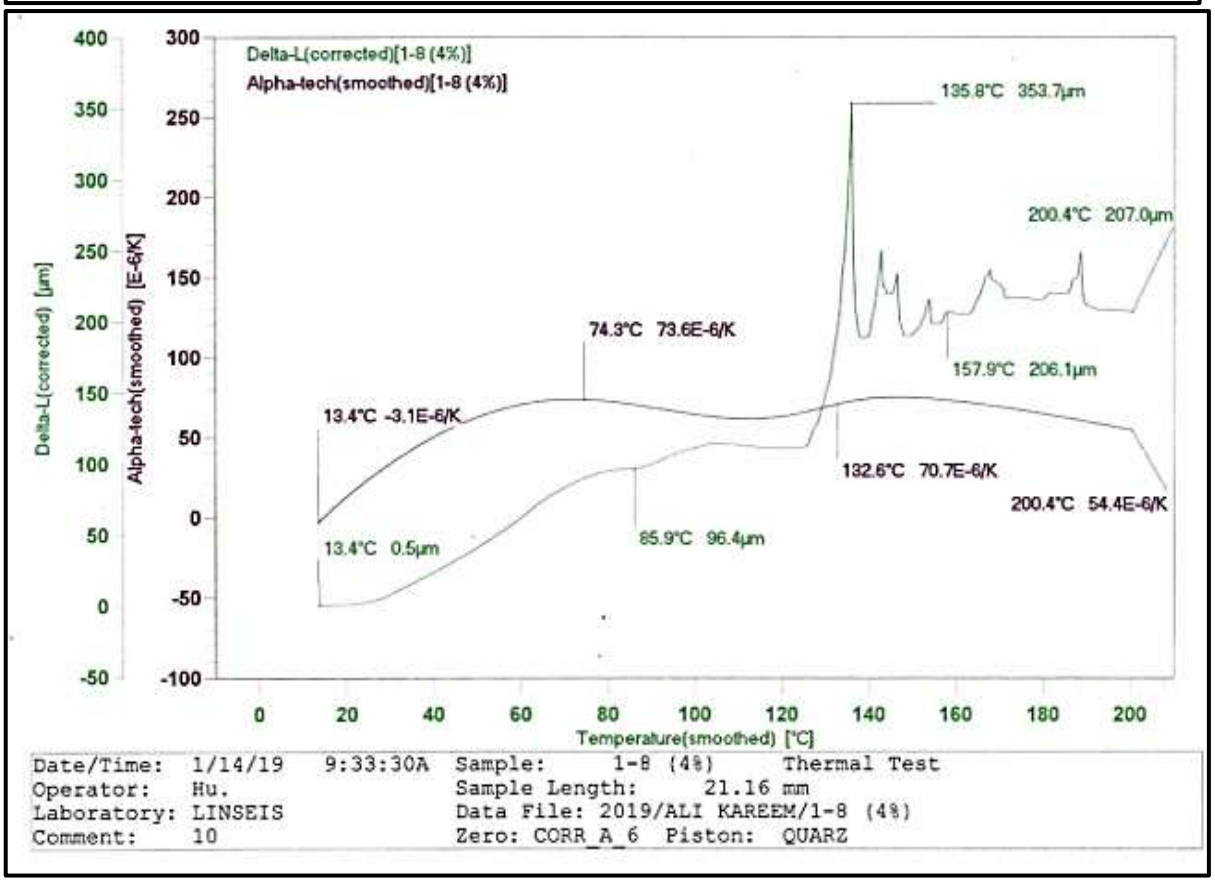


Fig. 5. Linear Thermal Expansion Coefficient with Percentages (PMMA / (CZT) NPs)




Delta-L(corrected)[1-7 (2%)]
Alpha-tech(smoothed)[1-7 (2%)]
160.2°C 188.4µm
63.8°C 84.5E-6/K
79.8°C 106.6µm
200.3°C -0.3E-6/K
18.2°C -2.8E-6/K
167.9°C 33.8E-6/K
127.1°C -71.8E-6/K
18.2°C 0.5µm
200.3°C -3.6µm
111.4°C -154.3µm
139.0°C -167.6µm
Delta-L(corrected) [µm]
Alpha-tech(smoothed) [E-6/K]
Temperature(smoothed) [°C]
Date/Time: 1/8/19 11:37:19 Sample: 1-7 (2%) Thermal Test
Operator: Hu. Sample Length: 20.99 mm
Laboratory: LINSEIS Data File: 2019/ALI KAREEM/1-7 (2%)
Comment: 10 Zero: CORR_A_6 Piston: QUARZ


Delta-L(corrected)[1-8 (4%)]
Alpha-tech(smoothed)[1-8 (4%)]
135.8°C 353.7µm
200.4°C 207.0µm
74.3°C 73.6E-6/K
157.9°C 206.1µm
13.4°C -3.1E-6/K
132.6°C 70.7E-6/K
200.4°C 54.4E-6/K
13.4°C 0.5µm
85.9°C 96.4µm
Delta-L(corrected) [µm]
Alpha-tech(smoothed) [E-6/K]
Temperature(smoothed) [°C]
Date/Time: 1/14/19 9:33:30A Sample: 1-8 (4%) Thermal Test
Operator: Hu. Sample Length: 21.16 mm
Laboratory: LINSEIS Data File: 2019/ALI KAREEM/1-8 (4%)
Comment: 10 Zero: CORR_A_6 Piston: QUARZ

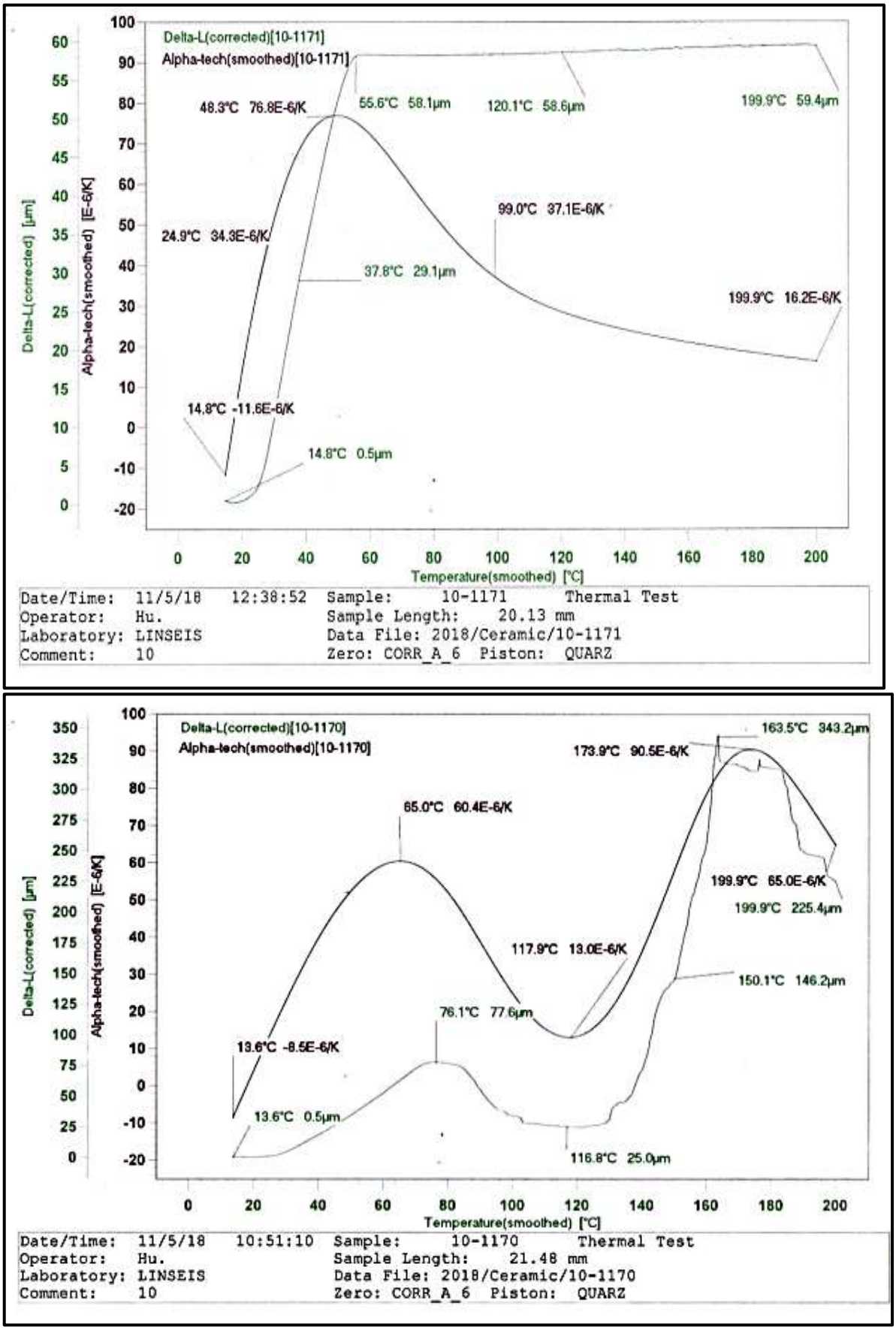


Fig. (6). (A),(B),(C),(D), (E) -Thermal Mechanical Analysis (TMA) Schemes -The Experimental Value of (PMMA / (CZT) NPs)with Temperature

The table (2) shows the linear thermal expansion coefficient (α)with the reinforcement material percentages the prepared and figure (7) shows a sharp decline in the linear thermal expansion coefficient (α) value of the composites compared to the base material (PMMA) as well as the ratio of (6 wt.% (CZT) NPs + 94 wt.% PMMA) is the least linear thermal expansion coefficient (α) temperatures at 60°C.

Table 2. The values of the linear thermal expansion coefficient (α).

Composites PMMA% + (CZT) NPs %	Thermal Expansion $\alpha \times 10^{-6}$ K^{-1}
100 wt.% + 0 wt.%	110
98 wt.% + 2 wt.%	84.5
96 wt.% + 4 wt.%	73.6
94 wt.% + 6 wt.%	60.4
92 wt.% + 8 wt.%	76.8

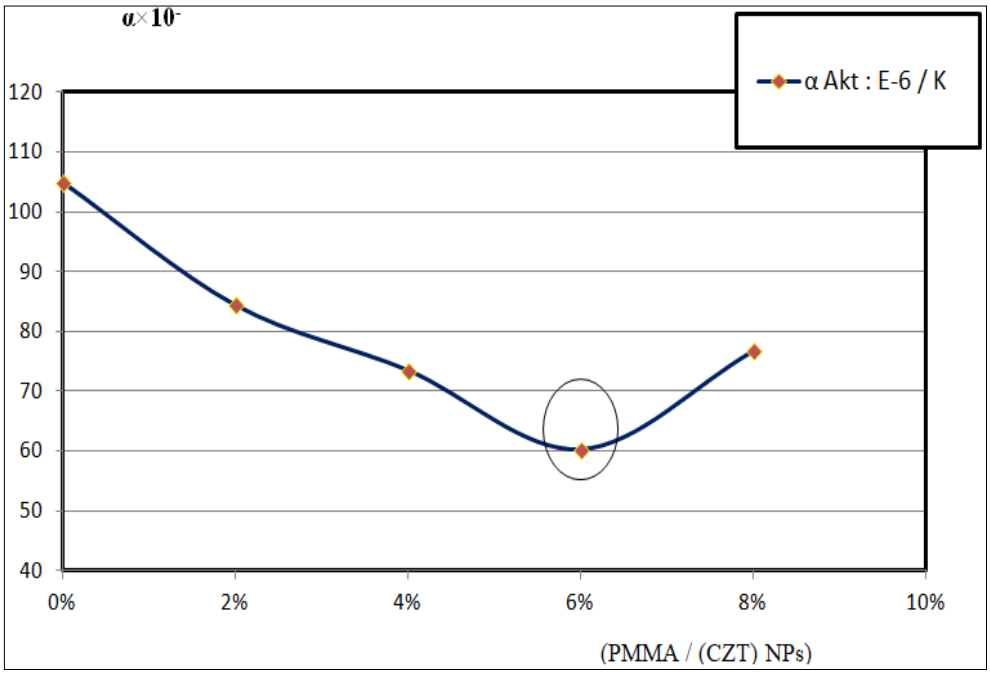


Fig. 7. The Thermal Expansion Modulus Variation with the Reinforcement Material Percentages

Conclusion

We can conclude that:

1. All prepared nanocomposites have a convergent coefficient of expansion at a temperature of (80) compared to the non-reinforced polymer basis sample.
2. Through the obtained practical results, it was found that the percentage less than 8% at a temperature of 60°C stabilizes the dimensions of the models and we get the lowest coefficient of thermal expansion specifically at a percentage of 6%.
3. All prepared nanocomposites decrease the coefficient of thermal expansion when reaching a temperature of 100% compared to the base material (PMMA) as it expands more and more at this degree.
4. Through the images (SEM), we note the formation a conglomerate semi-spherical appeared of a triple compound of the oxides involved in the reaction, and this indicates the merger occurring at the thermal reaction components of the (CZT) NPs.

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