Study the Contrast of Thermal Expansion Behavior for PMMA Denture Base, Single and Hybrid Reinforced Using the Thermomechanical Analysis Technique (TMA)

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Abstract. This research investigated the effect of adding two groups of reinforcement materials, including bioactive materials Hydroxyapatite (HA) and halloysite nanoclay and bioinert materials Alumina (AL_2O_3) and Zirconia (ZrO_2), each of them with various weight ratios (1,2,3,4 &5)% to the polymer matrix PMMA. The best ratios were selected, and then a hybrid was preparing Composite red from the best ratios from each group. Thermal properties, including thermal conductivity and Thermomechanical Analysis (TMA) technology, have been studied. The results showed that adding 3% Hydroxyapatite (HA) and 5% halloysite nanoclay to the polymethacrylate (PMMA) mer leads to an increase in thermal conductivity. It was also found from the Thermomechanical Analysis (TMA) technique that the change in length and the coefficient of thermal expansion (CTE) show a slight decrease in behavior compared to the single and hybrid reinforcements. On the other hand, it was found that the addition of reinforcing materials led to a decrease in glass transition temperature (Tg).

Keywords: hybrid composite, bioactive, bioinert, thermal conductivity, thermal mechanical analysis (TMA).

INTRODUCTION

Because of significant improvements in tribological and mechanical properties, hybrid polymer composites have become popular in the field of implant materials in recent years. When compared to their original equivalents, the addition of different compounds in powder form, such as glass fibers, carbon nanotubes, and carbon black, which function as reinforcement to the polymer matrix makes them more efficient materials in terms of mechanical, tribological, and thermal properties. In addition to improving other features, they are also cost-effective and simple to fabricate. This could aid in the development of new hybrid polymer matrix composites for use as implant materials. The addition of various compounds to the matrix improves mechanical and tribological properties due to terfacial bonding between the compound and the matrix, as well as biocompatibility, which is the primary requirement of implant material [1]. Because of its pleasing esthetics, ease of operation, low cost, and excellent oral environment stability, polymethyl methacrylate (PMMA) is still commonly used as a denture foundation material. However, one of the significant drawbacks of PMMA denture base composites is their weak mechanical properties, which restrict their application. Various micro-or nanosized fillers have been added to PMMA to allow for more clinical applications. Denture fracture remains an unsolved clinical problem, despite tremendous progress in this field [2]. Particulate composite materials are made up of a matrix of polymer resin and reinforcing particles. These composites have smaller particles than large particle reinforced composites. The particle diameter is usually measured in nanometers. In this situation, the particles are responsible for a significant portion of the load. The particles are employed to increase the matrix's modulus while decreasing its ductility. Nanoparticle reinforced composites are significantly simpler and less expensive to make**.** Bioceramics are polymer composite materials loaded with nanoparticles that can be used in dentistry and engineering to provide unique mechanical and physical properties while maintaining a low specific

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weight. Small ceramic particles have been shown to improve polymer tribological and mechanical characteristics [3]. Because it is a blend of oxide ceramics, Al_2O_3, ZrO_2, HA, and nanoclay has been employed as suitable filler material in polymer matrix composites. It improves the composites' physical and mechanical properties. Some researches which are accomplished in this field:

In (2013) P.Thomas, et al [12]. Studied structural, thermal, and property analysis for Poly(Methyl Methacrylate) (PMMA) and $CaCu_3Ti_4O_{12}$ (CCTO) composites. thermogravimetric (TGA), thermomechanical (TMA), differential scanning calorimetry (DSC), and Impedance analyzers were used. Thermal stability was shown to be better in composites than in pure (PMMA) and the glass transition (Tg) temperature of the polymer and the composite did not differ significantly.

In (2015) Abdil-Hameed R. Al-Saraf et al [11]. studied the coefficient of thermal expansion (α) and glass transition (Tg) behavior by using the thermomechanical (TMA) technique on unsaturated polyester resins (UP) containing weight percentages of phenolic Bakelite. It was observed that an increase in the proportion of phenolic Bakelite leads to a decrease in glass transition (Tg) while (α) increases at low temperatures while decreasing at high temperatures.

In (2016) Esra Kul, et al [10]. Studied thermalconductivity after adding powdered Ag, TiO_2, ZrO_2, Al_2O_3, SiC, nano-SiC, Si_3N_4, and HA-nano to PMMA, thermal conductivity was investigated. PMMA's thermal conductivity increased significantly after Si_3N_4, SiC, Al_2O_3, nano-SiC, TiO_2, ZrO_2, nano-HA, and Ag were added. Fillers made of Si_3N_4, SiC, and Al_2O_3 showed progressive increases in thermal conductivity.

The research's main goal is to evaluate thermal conductivity and study the behavior of glass temperature for single and hybrid composite materials with nanoparticle reinforcement to create hybrid composite samples for complete and partial denture base materials with excellent properties that will help to solve a variety of problems.

MATERIAL AND EXPERIMENTAL PART

Matrix polymer and reinforcement materials

Acrylic resin was employed as a polymer matrix in the sample preparation. It generally consists of a powder of polymethacrylate (PMMA) from Duracry® Plus self-polymerization and liquid methyl methacrylate monomer (MMA) supplied by (Acropars®, marlic) Marlic Medical Industries Co.

In this study, we used two types of nanomaterials as reinforcing materials. These were the types:

1- Bioactive: Nano Hydroxyapatite $Ca_5(PO_4)_3(OH)$ that is supplied from Shanghai Hualan Chemical Technology Co., Ltd. With a particle size of 40 nm and a purity of 96%, and halloysite nanoclay ($Al_2Si_2O_5(OH)_4$) from Sigma-Aldrich in the United States, with particle sizes ranging from 30 to 70 nm and a purity of 99.95%.

2- Bioinert: Nano Aluminum Oxide (Alpha-AL_2O_3) that is supplied from Houston SkySpring Nanomaterials, Inc., USA, from for particles smaller than 50 nm, the purity is 99.9%, and Nano Zirconia (ZrO_2) that is supplied Houston US Research Nanomaterials, Inc. USA manufactures Nano Zirconia, For particles smaller than 20 nm, the purity is 99.95 %.

Experimental part

From the previous research to be published, twenty-five samples were prepared, except for the control sample by using a Hand lay-up molding process as follows:

1- Powder (PMMA) mixed with hardener liquid (MMA) (2:1) in the volumetric ratio for 1 min at 25℃ ±3℃, obtained dough sticky state that was molded, after 20 min the dough hardened to obtain pure samples.

2- Powder of PMMA was mixed to powder of different weight ratios of reinforcement materials for 2.5 hours in a magnetic stirrer, the dry powder is mixed with the hardener according to step (1) to obtain single reinforcement samples. Each of the reinforcement materials used to prepare five samples (1,2,3,4&5)% Nano (PMMA/HA, PMMA/Halloysite NanoClay, PMMA/AL_2O_3, and PMMA/ZrO_2,), thus we get samples with single reinforcement materials.

From the previous research, we chose best reinforcement ratios (3% HA and 5% Nanoclay) for bioactive nanoparticles and (4% Al_2O_3 and 4% ZrO_2) for bioinert nanoparticles and depending on the tribology tests.

3- To prepare the hybrid composite samples, mix the best ratios together (dry powders) PMMA+ (3% HA + 5% Clay) and PMMA+ (4% AL_2O_3 + 4% ZrO_2) as in step (2) and prepare them as in step (1).

Each test has a distinct shape and size according on the American Society for Testing and Materials (ASTM). To ensure complete polymerization and a minimum quantity of excess monomer, all specimens are placed under IR lamp with a power of 100 watts and a distance of 30 cm for 48 hours, with continuous flipping of the specimens.

Thermal conductivity

The specimens were prepared in a circular shape (with a thickness of 4 mm and a diameter of 50 mm). Lee's method is used to measure thermal conductivity. It is the property of a material that indicates its ability to conduct heat. Conduction will take place only if there is a temperature gradient in the solid medium [4]. Figure (1) shows the dimension of samples for the thermal conductivity test.

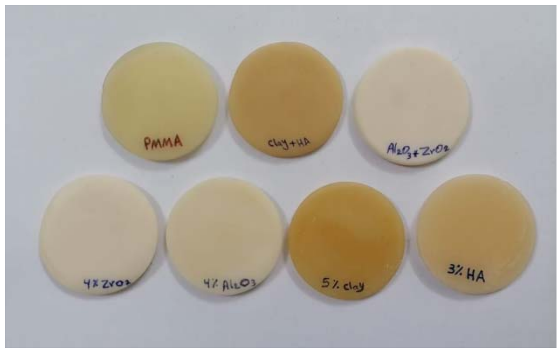

FIGURE 1. Samples of thermal conductivity test.

Thermalmechanical analysis (TMA)

When a polymer transitions from elastic to plastic state with a significant modulation in the free molecular volume, a TMA plot of the thermal expansion curve can be utilized to efficiently identify the glass transition temperature (Tg) for pure polymer or polymer composite materials [5]. TMA is a highly sensitive technology for determining the expansion and shrinkage of cross-linked or composite materials. In addition, the coefficient of thermal expansion must be calculated α (CTE). To conduct the (TMA) analysis, cylindrical shaped samples (L=30mm, D=5mm) were manufactured. TMA is defined as "a method in which sample deformation under non-oscillatory (static) load is determined as a temperature or time function while the sample is followed to a programmed temperature in a specified atmosphere" [6]. Linseis TMA PT1000 was used to conduct the tests. The heating rate is 2K°/min is the heating rate, and the final temperature is 140℃. Figure (2) show the dimension of samples for the thermomechanical test.

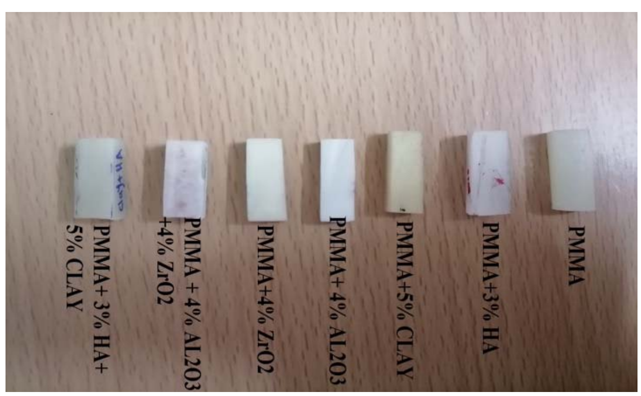

FIGURE 2. Samples of thermomechanical test.

RESULTS AND DISCUSSION

Thermal conductivity results

Thermal conductivity, or the ability to transmit heat, is one of the most essential thermal properties of dental materials. It is obtained by determining the rate at which heat can be transmitted through a given cross-sectional area of material specimens during a specific time interval. Table (1) shows the thermal conductivity values of PMMA-based nanocomposites. The thermal conductivity of the specimen improved significantly with the incorporation of 3% HA. The result is a value of (0.666) watt/m.C̊ which can give a higher thermal conductivity than non-filled (PMMA). Increases are mostly determined by various factors, including the filler's composition and how it is arranged throughout the matrix. However, grain size affects conductivity since the interface layer is inversely related to grain size, and these layers frequently serve to spread phonons, resulting in low thermal conductivity. Thermal conductivity is highly influenced by voids or pores caused by incomplete polymerization or casting process defects [7,8,9]. On the other hand, by creating a continuous path of the filler particles utilised as phonon transporters throughout the composite, particle aggregation may improve thermal conductivity [10]. Figure (3) show adding of different ratio nano particles single and hybrid on the PMMA.

TABLE 1. Values of thermal conductivity of PMMA based Nano composites.

Type of material	Thermal conductivity (Watt/ m.℃)
PMMA	0.490034
PMMA+ 3% HA	0.666995
PMMA+ 5% Clay	0.531282
PMMA+ 4% AL2O3	0.429684
PMMA+ 4% ZrO2	0.344378
PMMA+ (3% HA + 5% Clay)	0.421084
PMMA+ (4% AL2O3 + 4% ZrO2)	0.448678

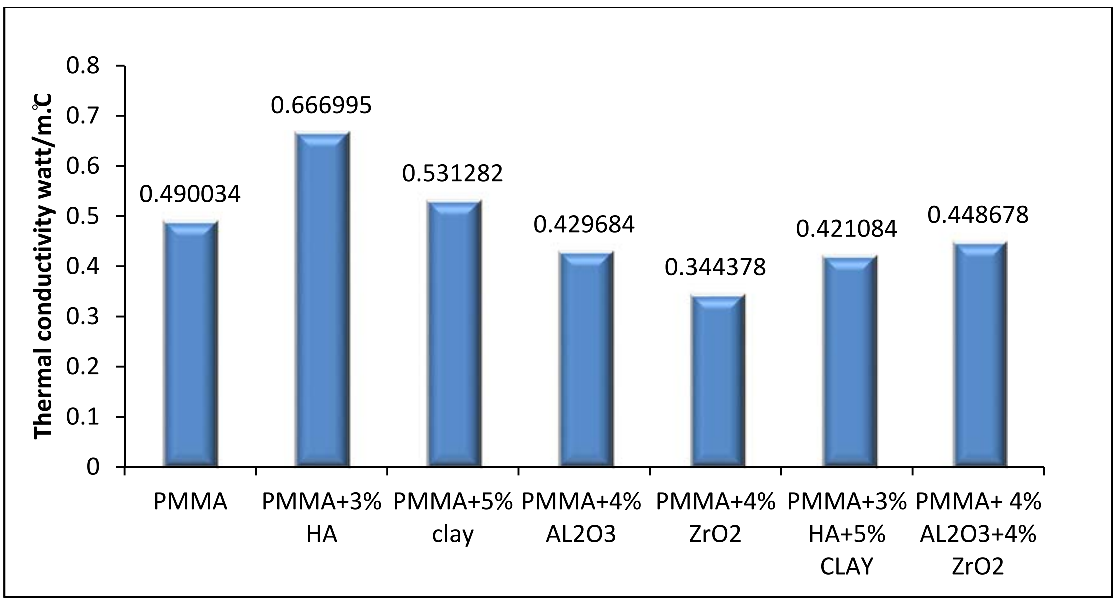

FIGURE 3. Thermal conductivity values of PMMA based Nano composites.

Thermal mechanical analysis (TMA) result

Pure and reinforced samples (single and hybrid) are subjected to thermo mechanical analysis in order to study the attitude of the change in length, percentage of elongation, and coefficient of thermal expansion with increasing temperature, which is important in many applications. From the figure (4) which shows the nonlinear attitude change in length (ΔL) as a function of temperature in the range of (20-160°C) for pure, single, and hybrid reinforced samples.

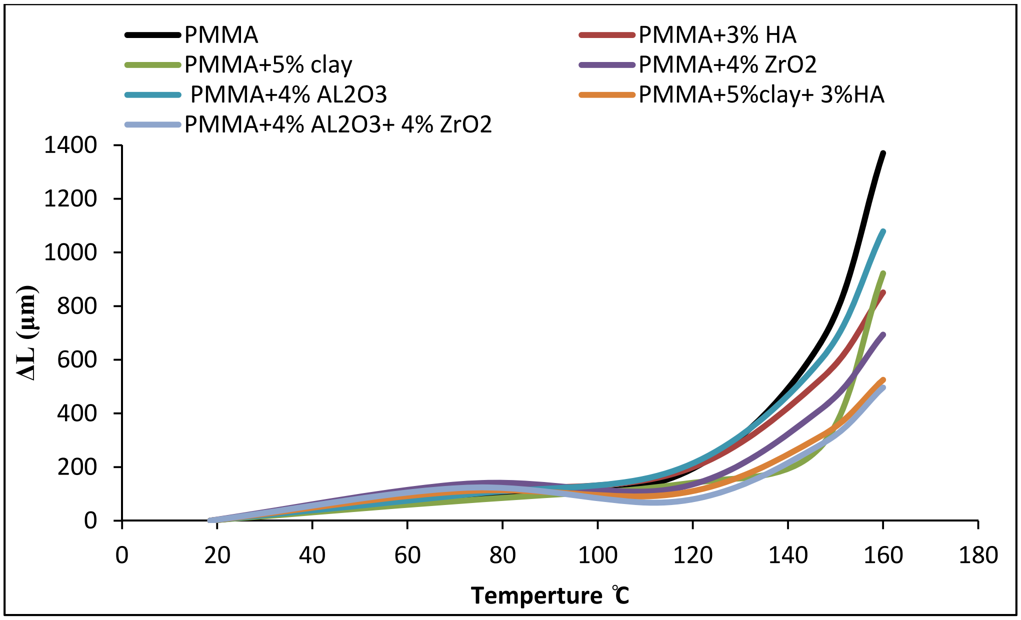

FIGURE 4. The length change of PMMA based Nano composites.

Temperature is the main factor in increasing the thermal energy of the molecules in the polymeric chain, which is accompanied by relatively different stress rates during the heating process, which leads to a plastic change that causes an increase in the length of the model [11]. Based on that, we notice in the figure a change the lengths according to the different types of materials and the single reinforcement ratios. As for the hybrid reinforcement, it appears clear from the figure (4) a decrease in the change the lengths of the samples. Figure (5) shows the attitude of the coefficient of thermal expansion (CTE) as a function of temperature in the range of (30-160°C) for pure, single, and hybrid reinforced samples. The CTE curves show transformations starting at (30℃), where α increases as the temperature rises, which is similar to crystalline materials. At the glass transition temperature, where the composite begins to convert into a sticky or flexible material, the attitude will change. When the temperature rises, the curve rises until it flattens out. This means the composite is undergoing non-reverse deformation. From the figure, we notice a decrease in the CTE of the hybrid composite. This may indicate the good adhesion between the polymer and the reinforcement nanomaterial [12,13].

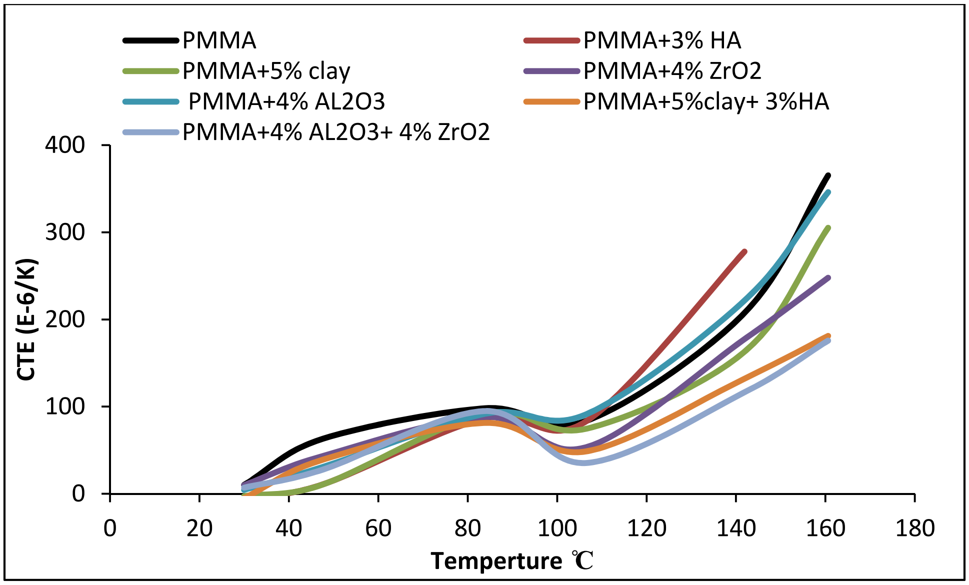

FIGURE 5. Coefficient thermal expansion of PMMA based Nano composites.

Table (2) shows the average glass transition temperature (Tg) of pure and reinforced samples single and hybrid composites recorded using (TMA). The appearance of a discrepancy in (Tg) with the different reinforcement ratios in PMMA was only an indication that the reinforcing materials acted as an impurity in the PMMA matrix. Figure (6) show glass transition of PMMA based Nano composites.

TABLE 2. Values of glass transition of PMMA based Nano composites.

Type of material	Tg (℃)
PMMA	106.6
PMMA+ 3% HA	105.4
PMMA+ 5% Clay	91.25
PMMA+ 4% AL2O3	99.3
PMMA+ 4% ZrO2	109.8
PMMA+ (3% HA + 5% Clay)	106.3
PMMA+ (4% AL2O3 + 4% ZrO2)	101.7

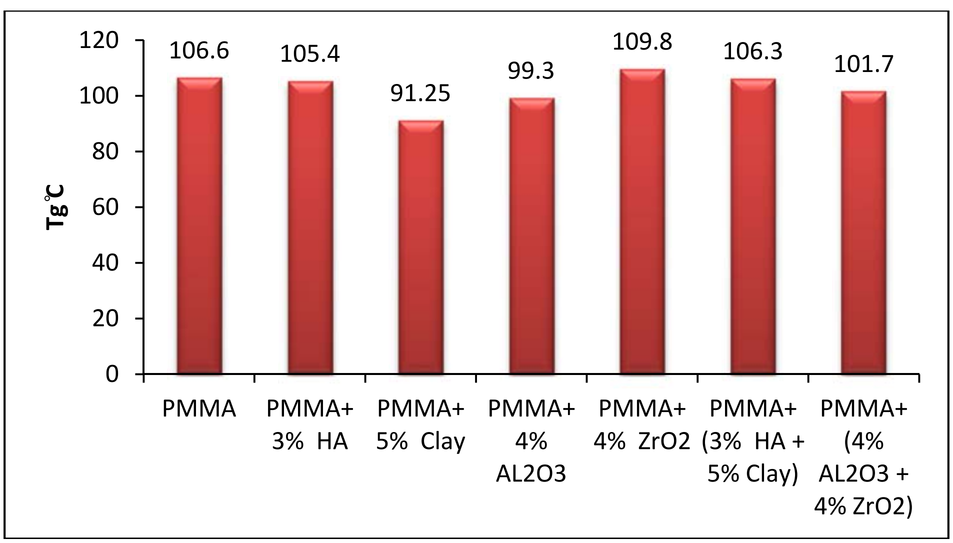

FIGURE 6. The glass transition values of PMMA based Nano composites.

CONCLUSION

In conclusion, the addition of single and hybrid reinforcement materials contributed in general to the decrease in thermal conductivity. The reinforcing materials exhibit a slight gradation of thermal stability with varied ratios in thermomechanical analysis test (TMA), and the samples have the optimum stability is at (PMMA+ 3% HA + 5% Clay) and (PMMA+ 4% AL_2O_3 + 4% ZrO_2), also the Glass transition temperature (Tg) Decrease with varied ratios reinforcement.

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