Thermal Characterisation of Poly(Methyl Methacrylate) Filled with Barium Titanate as Denture Base Material

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ABSTRACT: *Currently, most polymethyl methacrylate (PMMA) denture materials are radiolucent, and it is difficult to remove the fragments of dentures aspirated during accidents. The aim of this study was to investigate the possibility of using barium titanate ($BaTiO_3$) as a radiopacifier in PMMA. The formulation used in this study was composed of PMMA, $BaTiO_3$ (5,10, 15 and 20 wt%) and 0.5 wt% benzoyl peroxide (BPO) as an initiator, 90 wt% methyl methacrylate (MMA) as a monomer, and 10 wt% ethylene glycol dimethyl acrylate (EGDMA) as a cross-linking agent. The $BaTiO_3$ was treated by a silane coupling agent, (γ-MPS) prior to incorporation into the solid components (PMMA, BPO). Curing was carried out using a water bath at 78°C for 1.5 h. The thermal properties of the PMMA composite were evaluated using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). It could be observed that the density of the PMMA composite increased slightly after the filler was incorporated. In addition, filled samples showed slightly lower T_g values than the T_g value of the pure PMMA sample. The sample containing 20 wt% filler showed a higher degradation temperature than did the sample containing 5 wt% filler, which indicates that the former was more thermally stable than the latter. The TGA curves demonstrated that the degradation ratio increased more rapidly above 300°C. The storage modulus, E', was higher for the filled samples than for the pure PMMA sample.*

Keywords: Poly(methyl methacrylate), barium titanate, thermal characterisation, denture base materials, storage modulus

1.   INTRODUCTION

Currently, the acrylic resin poly(methyl methacrylate) (PMMA) is used almost universally for denture base fabrication.[1] The physical properties of the final polymer are important in the fabrication of polymeric denture bases as the cured polymer should be stiff enough to hold the teeth in occlusion during mastication and to minimise the uneven loading of the mucus. The denture

material should not creep under masticatory loads if good occlusion is to be maintained. Not only does the material have to have sufficient strength and resilience to withstand normal masticatory forces but it must also be able to withstand the sudden shock caused by impact forces.

The application of PMMA as an ideal denture base material is still restricted by a few limitations. One of them is the difficulty in achieving intrinsic radiopacity in the material, which is due to the constituent elements of PMMA. Presently, most denture plastics are radiolucent, and concern exists about the difficulty of removing fragments of dentures aspirated during accidents. Radiopacity is often achieved by the addition of a contrast agent, such as barium sulphate ($BaSO_4$). However, the presence of this radiopacifying filler affects both the mechanical and biological behaviour of PMMA composites at concentrations above 8%; moreover, samples require 29% $BaSO_4$ to be easily identifiable radiographically.[2,3]

The incorporation of filler into a polymer matrix can bring about changes in the mechanical and thermal characteristics of the resulting composite. One benchmark used to compare the thermal behaviour of composites is the glass transition temperature (T_g). Changes in the T_g as a function of filler content have been reported for polymer composites containing a wide variety of filler and polymer materials. Many researchers have reported an increase in the T_g as a function of filler content.[4] However, decreases in the T_g have also been reported.[5] Utilising the TGA technique, changes in the weight of a known amount of material are monitored as a function of temperature (or time) while atmosphere of the sample chamber is purged with an inert gas, usually nitrogen or a nitrogen/air mixture. In other words, TGA can provide quantitative information resulting from any processes that might cause detectable weight changes during the controlled heating process.

Major factors affecting the thermal, physical and mechanical properties of particulate (i.e., filler) reinforced polymer composites include the polymer structure and molecular weight, the filler type and volume fraction, and the interfacial state between the filler and the polymer. Various attempts have been made to reinforce PMMA denture base resins with a range of fibre types, including glass, sapphire whisker, aramid, carbon, nylon and polyethylene fibres. However, these fibres disrupt the homogeneous matrix of acrylic resin due to the poor interface formed between the fibres and the resin, adversely affecting the mechanical properties of the composite.[6] Other factors such as filler surface treatment and matrix modification also play an important role. Silane coupling agents contain two different reactive groups in their structure, one of which can be hydrolysed. These groups allow them to forge a strong interaction with polymer matrices and filler particles.[7] Carrodeguas et al.[8] reported that the

silanation of $BaTiO_3$ or $SrTiO_3$ particles provides a formulation with improved mechanical properties and injectability with respect to those of particles obtained with the untreated fillers.

Silanes are commonly used in dentistry in different applications to provide the opportunity for chemical bonding. The effectiveness of silane coupling agents has been well established by other researchers to improve the bond between inorganic filler and organic polymer matrix materials.[9–11] In addition, surprisingly, silanes do not exhibit intrinsic toxicity.[12]

Polymers used to construct a denture base ought to have a glass transition temperature (T_g) that is high enough to prevent softening and distortion during use. Although the normal temperature in the oral cavity varies from 32°C to 37°C, it should be considered that patients may sometimes drink hot beverages above this temperature and clean their dentures in very hot water despite being advised not to do.

A denture base is supposed to possess good dimensional stability to prevent the denture shape from changing over time. In addition to thermal softening, which may cause deformity, other factors such as the relief of internal stresses, continued polymerisation and water absorption may contribute to dimensional instability. The base material should ideally have a low specific gravity value as dentures should be as light as possible.

Barium titanate has already been investigated as a filler in bone cements,[8] but its use as a denture base composite is relatively new.[13] In general, our approach for enhancing the properties of denture base materials and their radiopacity is through the incorporation of $BaTiO_3$ filler, which can act as a radiopacity agent due to the high atomic numbers of Ba and Ti as well as the biocompatibility of $BaTiO_3$, which has already been demonstrated.[14] The aim of incorporating this filler is to improve the ability of PMMA to absorb X-rays to achieve a sufficient level of radiopacity and evaluate the effect of filler content on the thermal properties of the final material. Thereby, the effects of $BaTiO_3$ on the fracture toughness and performance of denture base materials were evaluated and published elsewhere.[13,15] The current study focused on the thermal stability of the $BaTiO_3$-filled PMMA, which is one of the prerequisites for dental materials. In the oral cavity, wide temperature fluctuations occur due to the ingestion of hot or cold food and drink. In addition, more localised temperature increases may occur due to the highly exothermic nature of the setting reaction for dental materials.

2. EXPERIMENTAL

2.1 Materials

The solid components consisted of PMMA with a high molecular weight (i.e., 996,000 GPC, Aldrich, U.S.A) plus 0.5% benzoyl peroxide (BPO) (Merck Chemical, Germany). The liquid component consisted of methyl methacrylate (MMA) (Fluka, U.K.), stabilised with 0.0025% hydroquinone, plus the cross linking agent, (10%) ethylene glycol dimethacrylate (EGDMA) (Aldrich, U.S.A). Barium titanate ($BaTiO_3$) in powder form (Across, U.S.A) with a particle size ranging from 0.4 μm and up to less than 1 μm was used as a filler. The silane coupling agent 3-(trimethoxysilyl) propyl methacrylate (γ-MPS) was supplied by Sigma-Aldrich. The function of the coupling agent was to enhance the interaction between the ceramic filler ($BaTiO_3$) and the organic matrix PMMA. The coupling agent's molecular formula is:

$$H_2C=C\,(CH_3)\,CO_2\,(CH_2)3Si\,(OCH_3)_3$$
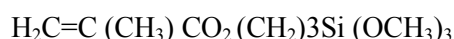
2.2 Filler Treatment

$BaTiO_3$ treatment involved the use of 200 ml of toluene and 10 g of $BaTiO_3$ powder and was performed according to the method described by Abboud et al.[16] The procedure commenced with the dispersion of the powder in toluene. Then, 10 wt% silane was added, and the resulting solution was refluxed for 15 h. Next, the solution was filtered to collect the modified powder. Subsequently, the powder was washed with 200 ml of fresh toluene in a Soxhlet apparatus for 24 h. The final product was then dried at 110°C for 3 h under vacuum.

2.3 Sample Preparation

Four different ratios (i.e., 0, 5, 10, 15 and 20% by weight) of treated filler were used. With the exception of the 0% filler, the fillers were added to the matrix (PMMA and 0.5% BPO). The planetary ball milling technique was employed to mix the solid phase (PMMA, BPO and filler) for approximately 30 min. Milling was continued for 4 min, followed by pausing for 3 min to prevent overheating and premature polymerisation. This cycle was repeated four times. The ceramic jars and balls must be cleaned with sand several times for a certain period, e.g., 30 min, to reduce the contamination of the powder mixture.

Powder to liquid (P/L) mixing was performed according to standard dental laboratory usage. After reaching the dough stage, the mix was packed into a mould and was pressed under a pressure of 14 MPa at room temperature for 30

min. The final polymerisation (curing process) was carried out using a water bath at 78°C for 1.5 h. The mould was then left to cool slowly at room temperature. The samples were then removed and polished with fine sand paper. The procedures adopted in this study are consistent with those of the prescribed standard method for preparing conventional denture base material in dental laboratories.[1]

2.4   Methodology

2.4.1   Determination of composites density

The test specimen density was determined according to the ASTM D 792 water-displacement method (Method A) using the following equation:

$$\rho = W_1 / (W_1 - W_2) \tag{1}$$

where W_1 and W_2 are the sample weights in air and water, respectively. The density of $BaTiO_3$ filler, as quoted by the manufacturer, is 6.08 g m^{-3}.

2.4.2   Weight and volume fraction determination

As some filler might be lost during processing, a polymer burn-off test or "ashing" was performed to determine the final weight fraction of the filler in the composite. Dumbbell-shaped specimens were randomly selected and burnt-off in a furnace at 600°C. The filler residue was weighed, and the corresponding weight fraction of the filler, W_f, was converted to the volume fraction of the filler, V_f. The following equation was used in the procedure:

$$W_f = \frac{\rho_f}{\rho_c} V_f \tag{2}$$

where ρ_c and ρ_f are the densities of the composite and the filler, respectively.

2.4.3   Thermal characterisation

2.4.3.1 *Differential scanning calorimetry (DSC)*

Thermal analysis was performed on composites to determine their glass transition temperature (T_g) using a Perkin Elmer DSC 7. Samples with a mass of approximately 10–15 mg were heated to 190°C at a rate of 10°C min^{-1}. This temperature was maintained for 1 min before subsequently cooled to 30°C at

$10°C \, min^{-1}$. The aim was to remove any processing history. The same steps were repeated for the second scan.

2.4.3.2 *Thermogravimetric analysis (TGA)*

Samples from all parts of a dumbbell specimen were collected and analysed using thermogravimetric analysis to confirm the filler content throughout the sample. This procedure was carried out with a Perkin-Elmer Pyris 6 TGA analyser at a heating rate of $20°C \, min^{-1}$ from $50°C$ to $550°C$ under nitrogen flowed at $50 \, ml \, min^{-1}$. The weight loss experienced by the samples as the temperature increased provided insight into the degradation rate and the filler content.

2.4.3.3 *Dynamic mechanical analysis (DMA)*

Samples were prepared from moulded plates and sectioned into rectangular beams measuring 3 mm × 13 mm × 60 mm (thickness × width × length) using a rotating band saw. The specimens were subsequently polished with sand paper and were then stored in sealed plastic bags and maintained at room temperature prior to analysis. Analyses were carried out with a Perkin Elmer DMA 7 analyser using the three-point bending mode.

3. RESULTS AND DISCUSSION

3.1 Effect of Filler Content on Density of Composite

The effect of filler content on the density of the PMMA matrix is shown in Table 1. It can be observed that the density of the PMMA composite increased slightly after the filler was incorporated. The slight increase in density can be attributed to the small amount of filler present in the composite. Furthermore, any rise in density is to be expected as the density of $BaTiO_3$ is higher than that of PMMA (i.e., $6.08 \, g \, cm^{-3}$). This result is consistent with the findings of Mohamed,[11] who reported that the density of composites increased with the addition of hydroxyapatite (HA) filler to PMMA.

Table1: Filler content of various formulations and its effect on the density of the PMMA composite compare to that of the PMMA matrix.

Formulations	Density (ρ_c) (g cm^{-3})	Measured W$_f$	Calculated V$_f$
PMMA matrix	1.18	0	0
PMMA + BaTiO$_3$ 5%	1.25	0.25	0.05
PMMA + BaTiO$_3$ 10%	1.29	0.48	0.1
PMMA + BaTiO$_3$ 15%	1.32	0.59	0.13
PMMA + BaTiO$_3$ 20%	1.36	0.89	0.2

The material used to produce a denture base should have a low specific gravity as the denture base should be as light as possible. Therefore, high denture density is considered undesirable, especially for the upper denture base, because a heavy denture base would be unstable in the patient's mouth and drop down during use.

3.2   Determination of Filler Content by Ashing

The exact filler content in the various formulations was determined by the weight of the remaining filler subsequent to the burning of the polymer component. The temperature was raised to 600°C to burn out the polymer phase. This temperature was maintained for 2 h before subsequently cooled to room temperature.

To determine the exact content, the filler was first cooled before weighing. The weight fraction (W$_f$) and composite density (ρ_c) were used to facilitate the calculation of the volume fraction (V$_f$) using Equation 2. The results of these calculations are listed in the table below.

3.3   Thermal Characterisation

The T_g and degradation temperature of the PMMA composites are compared to those of the PMMA matrix in Table 2. It can be observed that the T_g was slightly affected by the incorporation of the filler. The filled samples showed T_g values slightly lower than the T_g of the pure PMMA sample. This discrepancy may be attributed to the fact that there is no interaction between the filler particles and the polymer chains in the matrix. The interaction between polymer chains with the surface of particles can drastically alter the chain kinetics in the region immediately surrounding particles.[5]

Table 2: Glass transition temperature (T_g) and degradation temperature of $BaTiO_3$ filled PMMA composites compared to that of the PMMA matrix.

Formulation	Tg (°C)	Temperature (°C) at 5% wt. loss	Residual material at 450°C
PMMA matrix	99.9	251.9	0
PMMA matrix + BaTiO3 5 wt%	97.8	257.3	4.1
PMMA matrix + BaTiO3 10 wt%	95.98	259.6	7.6
PMMA matrix + BaTiO3 15 wt%	95.2	277.8	10
PMMA matrix + BaTiO3 20 wt%	94.8	279.9	12.9

As shown in Figure 1, the weight of the samples decreased up to a temperature of ≈ 95°C. This phenomenon is related to the evaporation of unreacted monomer.[17] In DSC, the glass transition of polymers is observed as a step increase in the heat capacity of a sample during heating due to an enhancement of molecular motion in the polymer. The measurement of the T_g of polymers is an important practical application of thermal analysis.[18]
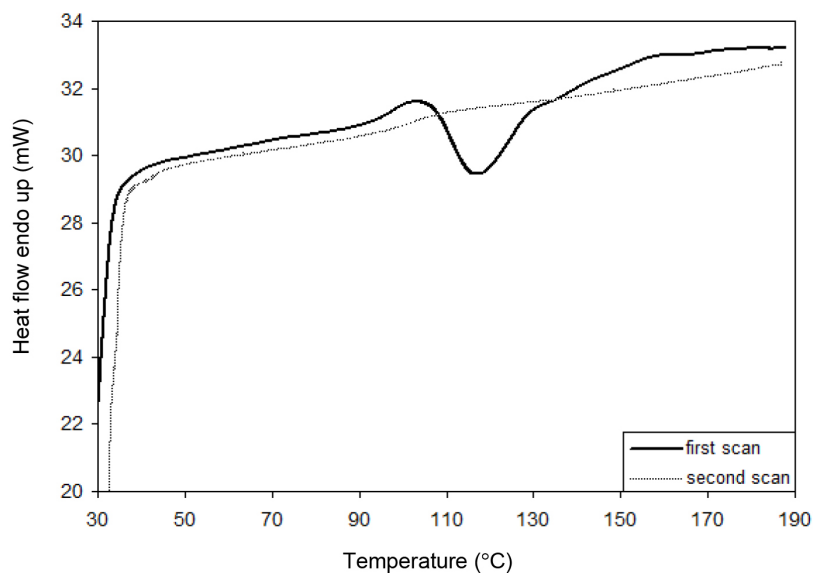

Figure 1: Typical DSC thermograms for PMMA matrix (first and second scans).

The DSC curves of the samples, for the first run, revealed a slight exothermic region occurring at ≈ 120°C (Figure 1). It can be postulated that this phenomenon is related to the evaporation of unreacted monomer at temperatures above the T_g of the MMA monomer. A similar observation was reported in the studies of the T_g of acrylic resin used in dentistry by utilising the DSC

technique.[11,19] The authors observed that the first scan showed an exothermic peak in the DSC thermogram, whereas the second scan showed no exothermic peak but only a glass transition pattern.

The TGA scans for various formulations of denture base materials are shown in Figure 2. It can be observed that little or no weight loss occurred up to a temperature of ≈ 250°C. However, immediately beyond this temperature, a sharp decrease in weight was observed, and at ≈ 450°C, almost complete weight loss was observed.

It is clearly evident that the samples exhibited different thermal degradation behaviours. It is interesting to note that the degradation temperature of the filled samples was slightly higher than that of the PMMA matrix. Moreover, the PMMA sample displayed no residual material formation at temperatures of up to 450°C. This behaviour is also indicative of the random chain scission processes the PMMA polymer undergoes during degradation.[20]
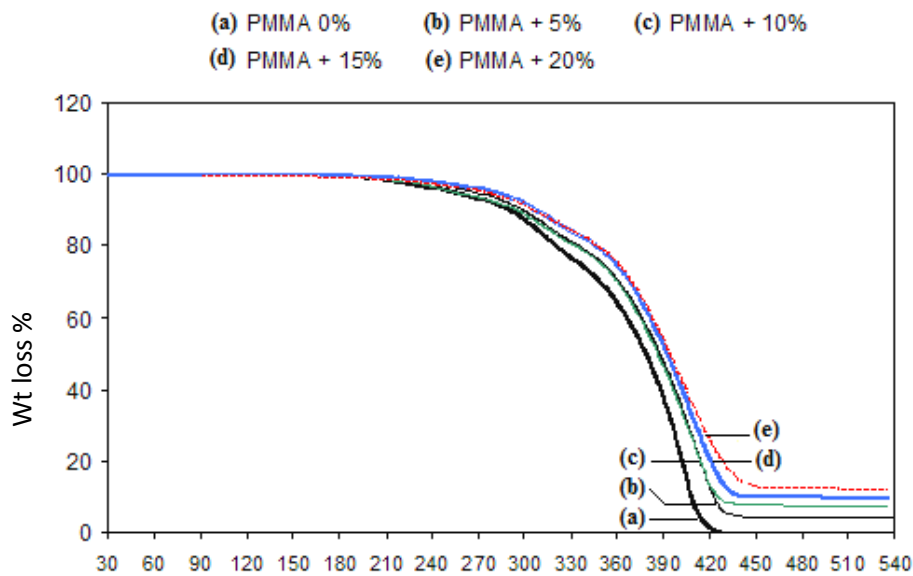

Figure 2: TGA curves illustrate the thermal degradation temperature of the PMMA composites compared to PMMA matrix.

All samples containing filler showed similar thermal behaviour. However, noticeable differences were observed with respect to certain characteristics. For instance, the sample with a filler ratio of 20 wt% showed a higher degradation temperature than that of the sample containing 5 wt% filler, which indicates that the former is more thermally stable than the latter. As

indicated by the TGA curves, the degradation ratio increased rapidly above 300°C. Hu and Chen[21] reported that there exist vinyl end groups in polymer chains of PMMA. These low-stability groups unzip the polymer chains radically through a chain transfer process. Compared to the polymer chain structure, the end groups exhibit weaker bonding and begin to degrade at approximately 220°C. As the temperature rises above 300°C, random scission constitutes the mechanism of degradation, and the depolymerisation rate increases due to main chain scission.

Figure 3 compares the DMA curves of the PMMA composites with that of pure PMMA. The storage modulus, E', was higher for the filled samples than for the pure PMMA sample. The storage modulus refers to the capacity of a material's elastic component to absorb and store energy. It is also associated with the rigidity and dimensional stability of a material under dynamic stress. The storage modulus curves were recorded at 1 Hz for the PMMA matrix and PMMA composites. As shown, the PMMA composites exhibited a higher level of rigidity than the PMMA matrix.
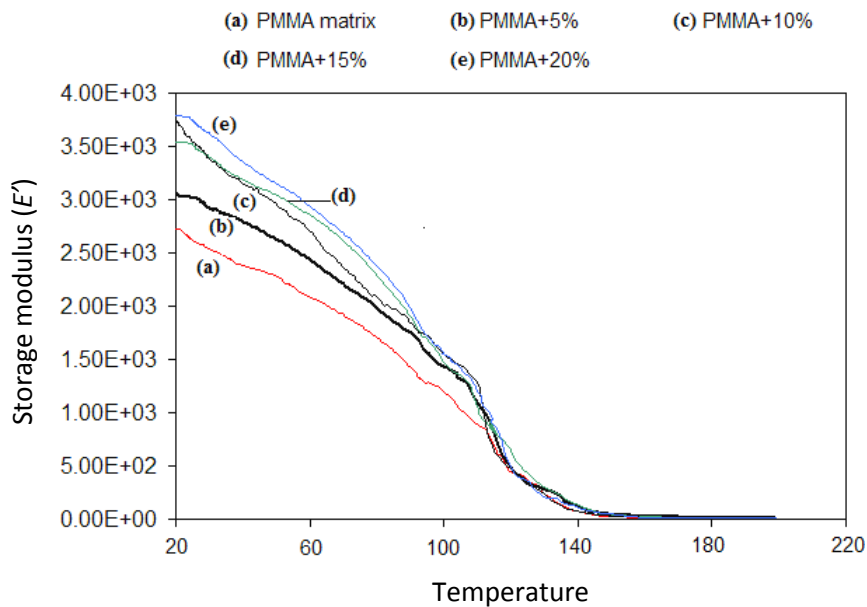

Figure 3: Variation of storage modulus with temperature for pure PMMA and PMMA composite with various formulations.

This rigidity increased as a function of the filler content. In all samples, it was observed that the storage modulus decreased as the temperature was increased. The curves show a general trend in which the storage modulus is much

higher below the T_g of the polymer but falls steeply up to 105°C. This behaviour is due to the T_g of PMMA as well as MMA monomer evaporation. The difference observed could be explained by the fact that the filled system is imperfectly dispersed because some extent of particle agglomeration always exists. Below the T_g, the polymer can exert large forces on the agglomerates due to its high modulus; therefore, a large extent deal of particle-particle motion should take place. However, above the T_g, the forces may not be sufficiently great to overcome the friction at contact points and break up the agglomerates.[22] A similar observation was reported by Kenny[23] in studying the storage modulus of high-density polyethylene/ultra-high-molecular-weight polyethylene (HDPE/UHMWPE) blends. Kenny reported that the storage modulus decreased as the temperature increased.

4.　　CONCLUSION

The density of the composites fabricated in this study was slightly increased by the incorporation of filler. However, the density of a denture base should be as low as possible to maintain the stability of removable prosthodontics, especially upper dentures, during use. It is interesting to note that the degradation temperature of filled samples was higher than that of the PMMA matrix. Moreover, increasing the filler content from 5 wt% to 20 wt% resulted in an increase in the degradation temperature and thermal stability of the resultant PMMA composites. Finally, the DMA test results clearly indicate that the rigidity of the materials rose as the filler ratio was elevated. On the other hand, the storage modulus decreased as the temperature was raised. Furthermore, a study on the effects of the curing cycle and those of time and temperature on the properties of similar composites, particularly their porosity, should be performed.

5.　　ACKNOWLEDGEMENT

6.　　REFERENCES

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