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Thermal analysis of dental materials

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Abstract: The mostly used TA techniques for materials characterization are differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). TGA is mainly used to examine the decomposition of materials by monitoring mass change with temperature. DTA and DSC are widely used for examining the phase changes of materials, where DTA measures temperature difference and DSC measures heat difference.

Keywords: Thermal analysis; DTA; TGA; DSC.

I. Introduction

Thermal analysis (TA) is a group of analytical techniques that measure properties or property changes of materials as a function of temperature. These techniques are mainly applied for the characterization and investigation of structure decomposition, thermal stability, and phase transition. Many TA methods have been developed for a variety of examination purposes and are distinguished from one another by the property they measure. The mostly used TA techniques for materials characterization are differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). TGA is mainly used to examine the decomposition of materials by monitoring mass change with temperature. DTA and DSC are widely used for examining the phase changes of materials, where DTA measures temperature difference and DSC measures heat difference. The term differential is used since changes in a specimen are measured with respect to a standard reference material (1).

1. Differential Thermal Analysis (DTA)

Differential thermal analysis measures the temperature difference of the sample under investigation and a thermally inert material (generally alumina) known as the reference against time or temperature. This temperature difference is then recorded while the sample and the reference are subjected to a controlled identical temperature program (heated or cooled) in an environment at a controlled uniform rate (same heat flow) (1).

1.1 Principle of DTA:

As the sample is heated, it undergoes reactions and phase changes it can be detected relative to the inert reference, energy is emitted or absorbed, and a temperature difference is detected between the reference and the sample. The temperature difference between sample and reference (ΔT) should be zero when no thermal event or reaction occurs in the sample, because of similar thermal conductivity and heat capacity between the sample and reference. But when the sample undergoes thermal event such as physical or chemical changes, ΔT will be generated and becomes different. When there is a physical change in the sample then heat is absorbed or released. For endothermic reaction, such as melting, dehydration, vaporization, loss of water or solvent the heat (energy) is absorbed and the temperature of the sample is decreased, so the sample would be at a lower temperature than that of the reference. While an Exothermic reaction, as crystallization, oxidation, polymerization the heat is released, and the sample temperature would be higher than the reference. These temperature differences between sample and reference produces a net signal, which is then recorded. A plot of the temperature difference reveals exothermic and endothermic reactions that may occur in the sample (2).

1.2 Sample presentation:

Almost any physical from of sample can be accommodated such as solid (amorphous or crystalline), liquid or gel, using various sample crucibles made from different materials (e.g.: platinum, aluminium). Sample size is usually small, a typical optimum sample weight of 50-100 mg (3).

1.3 Instrumentation:

DTA instrument is composed of fundamental components, figure 1. The sample is first loaded into a container and placed onto the sample pan or crucible (e.g., metallic or ceramic), figure 1. An equal quantity of inert material is placed in another container onto the reference pan. The dimensions of the pans should be nearly identical to be heated at a uniform rate. The sample and the reference weights must be equal, holders arranged symmetrically within a single heat source furnace and subjected to a common temperature program. The furnace and the holders are enclosed by an insulating material. As well, there is an electronic temperature regulator, programmer to ensure a constant rate of heating, and thermocouples for temperature regulation which are usually inserted into holders. The temperature difference between the sample and the reference are measured by the two thermocouples coupled in contact with the sample and with reference substance. The thermocouples are attached to an amplifier which converts the heat signal into an electrical signal and send the differential thermocouple outcome to the computer device to display in the form of a DTA curve or thermogram. The signal is only produced if a temperature deviation is observed; if the sample doesn’t undergo any reaction, no signal is generated as no temperature difference is observed (4).

Characteristics of DTA Curve:

The temperature difference of a sample when heating or cooling are shown in a DTA curve or thermogram, figure 2. DTA curve is a plot between differential temperature (ΔT) and temperature of reference (T). DTA curve may be endothermic (downward plot) or exothermic (upward plot) (2).

A downward plot is endothermic, DTA curve demonstrate that the sample temperature is less than that of the reference material, whereas an exothermic reaction is represented as an upward plot where the specimen temperature is greater than that of the reference. This temperature difference between sample and reference produces a net signal, which is then recorded. if there is no reaction happening in the sample material, then the sample temperature remains the same as that of the reference material (2).

A DTA curve can be affected by various factors. These could be either physical factors such as adsorption, crystallization, melting, and vaporization or chemical factors such as oxidation and reduction. It can also be affected by the characteristics of the sample, such as amount, shrinkage, particle size, or instrumental factors such as the recording system sensitivity.

1.4 Interpretation of DTA thermograph (2):

-Line AB: no reaction in the sample material, value of ΔT is zero.

-Point B: initial temperature point, the curve rises from the baseline due to the exothermic reaction and it forms a peak BCD.

-Point C: the process of heat is completed. Maximum temperature peak or heat value. The peak temperature is the characteristic of the sample material.

¬-Point D: Heat is decreased up to D point, final temperature.

-BCD area under peak has a direct relation with the amount of reacting material, and this amount can be determined by comparing the area of a characteristic peak of the sample with areas from a series of standard known samples analyzed under identical conditions.

1.5 Advantages (2,4):

1. Simple, Ease of use and adaptability.
2. Small sample size (tenth of a gram order), this allows the temperature to be homogeneous in the whole sample, avoiding a temperature difference along the sample that may affect results.
3. Both exothermic and endothermic reactions can be determined accurately.
4. DTA apparatus can operate over a wide temperature range, from −150 to 2400°C, using various heating and cooling programs. DTA feature is important for examining materials with high melting temperature such as ceramics and some metals.

1.6 Disadvantage (2,4):

1. Difficult to quantitatively obtain mass change during the test.
2. Complicated determination of phase transformation temperatures.
3. Low sensitivity and accuracy in quantity measurements of thermal analysis, when the absorbed or released heat during the measurements is not enough (too low) to be recognized; thus, the peaks associated with these thermal processes are not appreciated or are missed in the DTA curve.
4. Inherent limitation for its the development into a technique of high precision: The assumption of a constant value of the heat capacity of the sample and the assumption that the sample temperature is uniform at each time instant.

1.7 Applications (2,4):

1. Used to study the characteristics of materials, especially polymers it is based on measurement of properties like, melting point, decomposition temperature, crystallization and degree of polymerization can be assessed.
2. To distinguish exothermic and endothermic processes.
3. Qualitative identifications of material can be done by comparing the DTA of sample to DTA thermal curves of know materials.
4. DTA is widely used in the pharmaceutical and food industries.

2 Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a thermal analysis method which measures the difference in the amount of heat or the heat flow rate (⍰H) between the sample and an inert reference as a function of time or temperature, while both are subjected to a controlled temperature program. DSC measures the energy required to keep both the reference and the sample at the same temperature (3).

DSC differs fundamentally from DTA in that the sample and the reference are both maintained at the temperature predetermined by the program. DSC is a calorimetric method, where heat flow (uptake or release) and energy differences are quantitatively measured. While in DTA, the temperature of the sample is monitored with respect to a reference sample, DTA is a qualitative technique which measures temperature differences and do not provide any quantitative data for energy (5).

2.1 Sample presentation:

Samples are typically solid, can be in powder form such as metals, ceramics, organic and inorganic materials and predominately polymers. Liquid samples can also be tested. Sample size is very small, the sample weight in DSC experiments is in the range of 5 to 20 milligrams (6). For sample and reference crucible, A variety of sample pans or crucibles are available in different materials to handle different kind of samples measurements according to the material used to study, figure 3 (7).

The standard aluminum sample pans can be used for solids and powders that do not decompose or boil in the range of -170° to 600 °C. They are used with most routine applications, can also be used for nonvolatile solid samples such as metals, and polymer and inorganic materials provided that they do not react with aluminum. Platinum, copper, gold or alumina pans are used for samples which react with aluminum (e.g., biological samples). Also, they are used where high internal pressures are required or when sample of interest has a transition in high temperatures region (600-725°C), particularly useful in the specific heat capacity determination of liquids. In cases of undesirable metal-sample interactions occur, graphite pans are the method of choice(7).

2.2 Principle of DSC:

The basic principle of DSC, it studies what is the effect of heating on the samples. It measures the heat flow related to the thermal transitions in materials, as a function of time and temperature. Any event, such as loss of solvent, phase transitions, crystallization temperature, melting point, glass transition temperature of the sample, results in a change in its temperature. Thus, it provides qualitative and quantitative information about physical and chemical changes that involve endothermic (heat flow into sample), exothermic (heat flow out of the sample) processes or changes in heat capacity. The available DSC systems have a wide range of temperature capability, from -60 OC to >1500 OC (3).

2.3 Instrumentation:

DSC device may be one of two types: heat-flux DSC or power compensation DSC, the main difference is being mainly on their instrumentation design, depending on the principle of measurement used. The sample is placed in a crucible or a pan, then inserted in the cell of the machine, while the reference pan is empty. It’s in this cell where the test is conducted, and the data is collected. Having extra material in sample pan means that it will take more heat to keep the temperature of the sample pan increasing at the same rate as the reference pan (8,9).

2.3.1 Heat-Flux DSC is also called ‘‘quantitative DTA’’ as it measures the temperature difference directly and then converts it to a heat-flow, energy difference. The sample and reference are interconnected by a metal disk and placed in a single furnace, figure 3a. As the furnace is heated at a linear heating rate, the heat is transmitted to the sample and reference pan through the metal disk. The difference of the temperature between sample and reference is due to the changes of heat capacity (Cp) of the sample (the empty reference side heats faster than the sample side during heating of the DSC cell, so the reference temperature increases a bit faster than the sample temperature). This temperature difference creates the heat flow signal and is measured as a function of heat. (1,3)

2.3.2 Power-compensated DSC belongs to class of heat-compensating calorimeters. The heat to be measured is compensated with electric energy by increasing or decreasing an adjustable Joule’s heat. The sample and reference are placed in separate furnaces, where their temperatures are controlled and heated, by separate temperature controllers, and both have the same temperature figure 3b. As soon as changes in the sample occur, extra (for an endothermic effect) or less (for an exothermic effect), temperature differences between the sample and reference are compensated for by varying the heat required to keep both pans at the same temperature. The difference in power electrical input supplied to the sample and to the reference, to keep their temperatures as nearly the same as possible (the energy which is required to obtain zero temperature difference between sample and reference) is measured throughout the entire analysis. The energy difference is plotted as function of sample temperature (3,9).

2.4 Interpretation of DSC Curve:

The result of a DSC experiment is displayed in the form of a DSC thermograph, or a curve in which heat flow is plotted versus sample’s temperature. Concerning interpretation of DSC thermographs, The following phenomena are the most common obtained from a DSC experiment, no one sample would contain all the transitions shown in figure 4 (10).

(i) Glass transition temperature (Tg) which is the most common measured transition by means of thermal analysis techniques.

(ii) Crystallization (Tc), appearing as a well-defined exothermic process.

(iii) Melting of the specimen (Tm). Well-defined endothermic peak, since energy must be absorbed by the sample to get melted.

(iv) Heat of fusion ΔH which is determined by integrating the peak area.

(v) Cure reactions appearing as shallow and broad exotherms.

(vi) Moisture loss appearing as shallow and broad endotherms.

The area under the curve is directly proportional to heat absorbed or evolved by the reaction. The height of the curve is directly proportional to rate of the reaction.

On heating a polymer to a certain temperature, plot will shift a step downwards, there is more heat flow, where an increase in the heat capacity of the polymer occurs. This change in heat capacity that occurs at the glass transition, help to use DSC to measure a polymers glass transition temperature. After glass transition, the polymers have a lot of mobility, when they reach the right temperature, they will give off enough energy to move into ordered arrangements, the temperature at the highest point in the peak is usually considered to be polymer's crystallization temperature. If we heat polymer past its Tc, eventually another thermal transition will be reached, called melting Tm. When its reached, the polymers crystals begin to fall apart that is they melt. This means that the little heater under the sample pan must put a lot of heat into the polymer, to both melt crystals and keep the temperature rising at the same rate as that of reference pan. this extra heat flow during melting shows up as a big dip endothermic peak on DSC plot, figure 4 (11).

2.5 Advantages (2,4):

1. DSC is the most employed thermal analytical technique by the research community due to its low price, efficiency of handling and its relatively fast.
2. DSC is widely used to get information about glass transition temperature (Tg), melting point (Tm), crystallization temperature (Tc), the heat of crystallization (Hc), the heat of melting and heat absorbed or evolved during the cure reactions or decomposition reactions (9).
3. A very small amount of sample can be used and the sample present in any form can be tested in this technique.
4. A wide range of temperature control is possible.
5. 4. It can be used for studying many types of chemical reactions.

2.6 Disadvantages (2,4):

1. Inability to distinguish between samples having their thermal processes occur in the same temperature ranges (same melting points or glass transitions), the interpretation of the data becomes difficult due to overlapping of the peaks of phase transitions in the thermogram.
2. Interpretation of result is very difficult. It is highly dependent upon analyst experience. Subtle changes require detailed knowledge of chemistry and material information to understand.
3. The accuracy of the results decreases when trying to analyze nanomaterials or complex thermal processes.
4. DSC technique is sensitive to the heat-flow changes and the instrument calculates them as an average of multiple readouts. Using low heating rates or large quantities of samples could prevent this.

2.7 Applications (1,2,8):

1. Characterization of various kinds of samples for many applications can be done like polymers, pharmaceuticals, foods/biologicals, organic and inorganics chemicals and ceramics.
2. Material Identification: one of the primary uses of DSC, as to know if a polymer is semi crystalline or amorphous.
3. Phase transitions: determination of melting and crystallization points as well as phase transitions by measurement of the change of energy over temperature. DSC is widely used for examining polymeric materials to determine their thermal transitions. Important thermal transitions include the glass transition temperature (Tg), crystallization temperature (Tc), and melting temperature (Tm) as well as determining special properties of polymers such as crystallinity, curing status, polymer content, and stability.
4. Determination of Phase transformation and phase diagrams: the curve peaks of DSC reveal solid-state phase transformations over a temperature range.

3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as a sample is subjected to a controlled temperature program in a controlled atmosphere. It measures the change in weight of the sample during the process of heating or cooling. It is used to measure the phase changes, glass transition, and melting point. TGA is a powerful technique for the measurement of thermal stability of materials including polymers(4).

3.1 Sample presentation:

The sample pans (ceramic or platinum) can accommodate liquids, powders, films, solids, or crystal. The sample weight influences the accuracy of weight loss measurements, weight of the sample is up to 1g, typical sample is in mg, up to 50 mg of material is desirable in most applications and for volatile materials its around 20-100 mg of sample (12).

3.2 Principle of TGA:

TGA determines the amount and the rate of weight change of a substance with respect to temperature or time in controlled programmed conditions. The mass change profile (mass loss or mass gain) is continuously monitored and recorded as the sample is subjected to a controlled heating or cooling environment. TGA is used principally in the research and development of various materials to obtain knowledge and examine the strength of the material at a given temperature (thermal stability) as well as their compositional properties (e.g., fillers, polymer resin, solvents). Additionally, it is used to understand certain thermal events such as absorption, evaporation, decomposition, oxidation, and reduction, such events could bring drastic change in the mass of the sample.

3.3 Instrumentation:

TGA is conducted on an instrument referred to as a thermogravimetric analyzer, where mass, temperature, and time are considered its basic measurements. A thermogravimetric analyzer continuously measures mass while the temperature of a sample is changed over time. The fundamental instrument needed for TGA is a precision balance "Thermobalance" with a furnace designed to linearly increase temperature over time, which is regarded as the heart of a TGA unit (13).

Main components of TGA apparatus:

1. Highly sensitive scale, microbalance to measure weight change. The balance is located above the furnace and is thermally isolated from any thermal effects, to maximize the sensitivity, accuracy, and precision of weighing.
2. Sample holder or crucible could be made from platinum, aluminum or ceramic, it is necessary that the crucible should possess at least 100^oC higher thermal stability compared to experimental temperature conditions. The crucible holds the sample supported by the precision balance and located inside a programmable furnace.

3. Furnace with temperature programming facility, that is heated or cooled during the experiment, to control the temperature of the sample. The furnace can scan over a wide range of temperature 25 – 1200 ^{0}C and it is constructed of quartz. The balance and the furnace assembly are the two key components of thermobalance.
4. Facility to supply the gas, for providing inert atmosphere or oxidizing environment and an infrared spectrometer added to TGA allows identification of gases generated by the degradation of the sample.
5. Computer for observing the weight and temperature changes, where the balance is calibrated in a manner that a change in weight of the sample produces a proportional electrical signal. The computer collects, stores this electrical signal and converts it into weight or weight loss, which is then plotted on the thermal curve and calculate the weight-loss fraction or percentage.

3.4 Interpretation of TG curve

Data are obtained by plotting a graph between the mass change as a function of the temperature or time and are interpreted from TGA curve or thermogram, figure 6. This example of TG curve exhibits a single stage of decomposition.

In the curve, “Ti is the Initial Decomposition Temperature” represents the temperature at which the onset of decomposition is initiated and point at which the weight change attains a magnitude that can be detectable by a thermobalance.

“Tf is the final decomposition temperature” represents the temperature at which the decomposition reaction is completed and the point at which the weight change attains a maximum and cannot change further.

The values of Ti and Tf depend on the thermal stability of the sampling analyzed. The temperature at which no weight loss takes place indicates stability of the material (13).

The TGA curve is classified into the following seven different types based on their shapes, figure 7 (13).

Type i: No mass change over the entire temperature range used for analysis; the sample is considered stable. It may be because the thermal stability of the sample is higher than the temperature range of the sample.

Type ii: There is a mass loss region, which is then followed by a constant plateau line. This could be due to evaporation of volatile product(s) during drying, or polymerization. The sample decomposed due to dehydration.

Type iii: Single stage of weight loss or decomposition temperatures (Ti and Tf). the sample decomposes in one sharp step.

Type iv: Samples decompose in multi-stages, with relatively stable intermediate products.

Type v: Multi-stage decomposition with no stable intermediary. Heating rate may affect the plot, where at slow heating rate, type (5) resembles type (4) curve.

Type vi: Sample weight is increased, due to certain surface reactions (such as oxidation of metals) with atmosphere.

Type vii: Multiple reactions one after the other with respect to a rise in temperature. The increase in weight is due to the surface oxidation reaction, whereas the decrease in weight with further rise in temperature corresponds to the decomposition process, due to reduction. (Surface oxidation reaction followed by decomposition of reaction products).

3.5 Advantages (2.4):

1. It is a convenient and time-saving technique, can be easily implemented where any type of solid can be analysed with minimal sample preparation requirements.

2. It has high accuracy of balance, high precision of temperature controlling system and atmospheric conditions, allowing uniformity of the procedure.
3. Continuous recording of weight loss as a function of temperature ensures equal weightage to examination over the whole range of study.

3.6 Disadvantages (2,4):

1. TGA can study process which accompanies a mass change. Chemical or physical process which are not accompanied by the change in mass on heating or with no volatile product could not be studied. Limited to samples that undergo weight change.
2. It is very sensitive to any change, TGA is dependent on procedural details such as furnace heating rate, the atmosphere inside the furnace, sample size, or weight
3. Interpretation of the result is not always straightforward but rather complex.
4. Operation requires high control over temperature.

3.7 Applications (2,4,13):

TGA is particularly useful for the following material characterization determinations:

1. Thermal stability: is described as the ability of a material to maintain constant characteristics when exposed to heat. TGA is used to evaluate the thermal stability of a material and is mainly used for polymers. In a desired temperature range, if a material is thermally stable, there will be no observed mass change. Negligible mass loss corresponds to little or no slope in the TGA trace.
2. Compositional analysis for samples and multi- component materials: Upon increasing the temperature of a sample, it undergoes weight loss. The weight loss profile remains significant for chemists to determine the composition of a sample so that it is possible to understand the reaction steps involved in the decomposition process and to identify an unknown compound present in the sample or examine complex materials by removing or decomposing their constituents. And also evaluate thermal decomposition mechanisms of polymers which indicates evaporation or decomposition processes of a substance.
3. Corrosion studies: TGA can be used to analyze oxidation or other reactions with different reactive gases or vapours.
4. Evaluation of moisture and volatile contents in the sample materials lost during chemical reactions, for samples such as nanomaterials, polymers, polymer nanocomposites, fibers, paints, coatings, and films.
5. TGA can estimate lifetime, shelf life of a product.
6. TGA provides quantitative measurement of mass change in materials associated with transition and thermal degradation.
7. The TGA can determine the quantity of a filler in a polymer, to estimate the additive content.

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