Biomaterials Journal
http://www.biomatj.com
Online ISSN: 2812-5045

Type of the Paper (Review Article)

Characterization of Dental Materials: Time-of-Flight Secondary Ion Mass Spectroscopy, Dynamic Mechanical Analysis, and-Focused Ion Beam

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Abstract: Characterization of dental materials is necessary for understanding and identifying the materials composition, structure, and properties. Many characterization techniques and methods are used for surface characterization analysis, evaluation of dynamic moduli, and investigation of the materials surface and subsurface through electrons and ions. Time-of-flight secondary ion mass spectroscopy technique is used for materials surface characterization, analysis of surface molecules and surface-mediated reactions. Dynamic mechanical analysis is a technique that measures the complex moduli and study the viscoelastic properties of solids. Focused Ion Beam technique is used in imaginging of materials' surfaces using ion beams, deposition of materials such as platinum and carbon onto the materials surface, and milling of materials.

Keywords: *ToF SIMS; Dynamic mechanical analysis; complex modulus; surface characterization; Focused Ion Beam.*

Citation: ***Yasmeen S. Mahmoud . Characterization of Dental Materials: Time-of-Flight Secondary Ion Mass Spectroscopy, Dynamic Mechanical Analysis, and-Focused Ion Beam.*** *Biomat. J., 2 (2),46 – 52 (2023).*

https://doi.org/10.5281/znodo.5829408

Received: 10 February 2023
Accepted: 20 February 2023
Published: 28 February 2023

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1. Time-of-flight secondary ion mass spectroscopy (ToF SIMS)

ToF SIMS is a qualitative technique used for the surface characterization analysis in materials science as it provides information about entire or fragments of molecules from the outermost surface of the sample. It is applicable to any surface-mediated reactions such as sorption, redox, dissolution, precipitation, coprecipitation, catalysis, etc [1].

ToF SIMS is based on measuring the mass to electric charge ratio of a given ion (m/z). From the weight to charge ratio of an ion, it is possible to determine the molecular weight of the entire or fragments of the molecule. The ionization methods are chosen such that the charge (z) is 1 for most ions, so when interpreting the spectrum, it can be assumed that m/z corresponds simply to the molecular weight of the ion [2].

1.1. Basic principle of ToF SIMS:

ToF SIMs uses a pulsed ion beam (commonly Cs, Bi, or Ga) that penetrates 1–2 nm under the surface, to remove molecules. The molecules removed from the atomic monolayers of the surface (dislocated secondary

ions with positive or negative charge), are accelerated into a "flight tube" until reaching the detector which detected the molecular mass by measuring the time of flight [1].

1.2. Types of Secondary ion mass spectroscopy (SIMS) analysis:

1.2.1. Static (SSIMS):

The incident ion on the surface (about 10-10 A) generates the ejection of secondary ions coming from the first or two layers of the material surface and the damages on the surface can be ignored because they are minimal. When insulating materials like polymers are studied under SSIMS, some charging problems on its surfaces can be observed, and this problem affects the analysis, decreasing the sensitivity.

1.2.2. Dynamic SIMS:

The incident ion on the surface (about 10-7 A) causes a rapidly eroded surface and the information obtained is not exactly from the first layers (1–2 nm). For that reason, dynamic SIMS is ideal to get information from depth profiling.

1.3. Disadvantages of ToF SIMS:

- Due to the high sensitivity of this technique, only high purity solvents should be used.
- It is a destructive technique due to the impact of the ion beam that destroys the first monolayers on the surface's sample.
- This equipment has limited optical capabilities; sometimes has difficulties in collecting positive or negative ion data.
- Depending on the nature on the sample, the analysis can vary between 30 min and 5 h
- ToF SIMS is a qualitative technique able to determine fragments of the material exposed to analysis. The presence of a peak of specific element does not represent a quantitative information [1, 2].

1.4. Advantages of ToF SIMS:

- It can determine elemental and chemical mapping on a sub macroscale by surveys (of positive and negative ions (positive and negative spectra), individual isotopes, and molecular compounds) of all masses on materials science.
- Samples such as metals, ceramics, organic and biological materials, polymers, biomaterials, composites can be analyzed distinguishing species of similar nominal mass.

- The traces of elements are detected in the order of ppm (parts-per-million (10−6)) for most chemical species[1].

2. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) is an important materials characterization tool which measures the complex elastic moduli of solids. Static force-assisted mechanical studies cannot resolve the complex moduli of a material. There are different moduli based on the type of deformation, such as Tensile modulus, Compressive modulus, and Shear modulus [3].

The complex modulus of a material contains both storage (recoverable energy, elastic) and loss (thermally dissipated, viscous) parts. The study of the solids response to dynamic stimulus is important in different fields where the frequency-dependent modulus variations is an important measure such as paint industry, adhesive development, plastic hip joints and dental fillings, contact lenses, heart valves, mechanical dampers, and airbags [3].

Evaluation of complex modulus is important to study the viscoelastic properties of a solid, where no material is ideally elastic (ideal solid) or viscous (ideal liquid) in nature. As the applied frequency becomes higher, the material becomes more like a solid (higher storage modulus) and at lower frequencies liquid-like (lower storage modulus) behavior will dominate. Moreover, the modulus depends on temperature, at higher temperatures the material behaves like a liquid [4].

2.1. Uses of DMA:

- It can give information about phase transitions in materials such as polymers. Phase transitions occur due to inter-molecular rearrangements as a response to the applied frequency or temperature[4].

- It can be used to study composites and mixtures, and the complex interactions among their constituents.

- DMA is an efficient method to resolve stress or strain hardening or softening due to cyclic loading.

- For example: Certain composites matrices such as poly(dimethylsiloxane) impregnated with vertically aligned carbon nanotubes show such self-strengthening under cyclic loading because of complex interactions between matrix materials and nanostructures [5, 6].

- DMA is helpful in the assessment of materials properties in terms of operational temperature, load, frequency, other external parameters, and inter-material interactions.

The present DMA based experiments can simulate the real-time performance of materials. They measure the strain of as small as 1 nm with a load (force) range of 0.0001N– 18 N in a

wide temperature range (150 C–600 C), in different humid conditions, and can mimic the mechanical relaxations of solids in different environments. An advanced tool in DMA can conduct dynamic mechanical studies in liquid environment. They can be used to study or simulate the performance of biological membranes in actual physiological conditions [4].

2.2. Basic working principles of DMA:

The viscoelastic behavior of a material is evaluated as a function of time, temperature, and frequency. A sinusoidal oscillatory force is applied to the material and the resulting deformation or strain is measured in response to the applied stress in the linear viscoelastic region of the material. It is important to evaluate the linear response of the material before the dynamic force (strain) based experiments. The amplitude of the dynamic perturbation should be so small that it should not go beyond the linear Hookean region of the material [4, 7].

The response of the viscoelastic material to the dynamic stimulus will not be in-phase with the stimulus. The phase difference is 90° for a pure viscous material**,** 0° for a perfectly elastic material, and intermediate for a viscoelastic material. By evaluating the phase lag (δ), the material's properties such as the ability to flow (viscosity) and the stiffness (modulus) from recovery could be calculated. The loss modulus which measures the energy dissipated as heat and represents the viscous portion. The loss factor tan δ determines whether a material presents a predominantly elastic or viscous response when subjected to load while in service. For a material with tan δ greater than 1, the viscous component predominates [8].

The sample is placed in a holder and the dynamic force is applied using a force motor. The displacements are measured by linear variable differential transformer or optical encoders with high-precision for measuring linear displacements over a wide range. The temperature is an important parameter which affects the mechanical properties of viscoelastic materials such as polymers, therefore the sample chamber should be kept at a constant temperature [4, 7].

2.3. Different DMA modes:

a) Multi-frequency:

The multi-frequency mode evaluate stress/strain variations as a function of frequency. It is used to determine the glass transition (Tg) and melting temperatures (Tm) of polymers. At higher frequencies, the material has solid-like behaviour whie it becomes liquid-like at lower frequencies.

b) Multi-stress/strain:

Varying stress/strain is assessed while frequency is held constant.

c) Controlled force/strain rate:

Stress or strain is changed at a constant rate. The Young's modulus is calculated from the linear portion of the curve. Then, it enters the plastic region until failure. The area under the curve represents the energy required to break the material which is the toughness of the material [9].

d) Iso-strain mode:

The strain is held constant during a temperature ramp. It can be used to measure the shrinkage force in films and fibers.

e) Creep–recovery:

Creep testing is performed through application of a constant stress to the sample and the deformation is measured as a function of time. After the removal of stress, the material is allowed to relax, which is called a recovery test [7].

f) Stress relaxation:

Stress relaxation is the reverse of creep recovery test. The strain is held constant, and the stress is recorded as a function of time [3].

3. Focused Ion Beam (FIB)

Biological 3D imaging is made by Serial-Section TEM, in which sequential sections of resin-embedded samples are imaged. This technique allows high-resolution imaging in x- and y-planes, while the z-resolution is limited by the slice thickness. This 3D reconstruction suffers from poor resolution, as well as from distortion and shrinkage of the tissue due to the larger electron dose. Another method for obtaining 3D images is the use of Serial block face SEMs. This method destroys the sample, and it is prone to charging artifacts and slicing artifacts such as knife marks, holes, folds, compression and/or stretching[10].

Poor control over the thickness of each slice can also generate artifacts in the 3D volume, resulting in inaccuracies in the high-resolution 3D reconstruction of features in the sample. Therefore, 3D imaging artifacts can be reduced or eliminated by milling of the sample using a focused ion beam (FIB) [10]. FIB systems are similar to SEM, the only difference is the use of an ion beam rather than the electron beam for scanning the sample surfaces. A focused beam of metal ions is generated by a liquid metal ion source (LMIS) which can produce ions of ≈5 nm in diameter. Gallium is the most preferred LMIS because of its low melting point, low volatility, and low vapor pressure[11].

When Ga is heated the liquid metal flows down a needle tip to which a voltage is applied. This voltage results in Ga+ ions emission and the resulting beam is accelerated, directed through several apertures, and focused through a series of lenses at the sample surface[11]. Ga+ ions are heavy, and when they meet atomic nuclei in a sample, they cause efficient 'sputtering' (i.e.,

removal of the substrate) at a rate that is dependent on the material itself, and on the beam parameters [10].

3.1. Applications of FIB technology:

a) Scanning Ion Microscopy

When a solid sample is irradiated with focused Ga ion beam, secondary electrons are generated and emitted from the surface can be detected and observed as images. The secondary electrons produce a contrast depending on the crystal orientation of each grain producing a Scanning Ion Microscope (SIM) image. By observing SIM images of metal polycrystals, it is possible to obtain knowledge about the size and distribution of crystal grains. However, resolution is inferior to SEM images (SIM: 4nm, SEM: 0.5nm)[12].

b) FIB-SEM dual-beam microscopy:

FIB-SEM forms a powerful tool for 3D imaging. The SEM column (usually oriented vertically) and an FIB column oriented 45°–55° with respect to the microscope column have their own systems of lenses, apertures, and electronics, and generally operate independently of each other. A sample placed in the evacuated FIB-SEM instrument chamber can be interrogated by either of the beams, or by both beams simultaneously when placed. This allows the user to mill (with the FIB) and image (with the SEM) a specific location on a sample without tilting or moving the stage [13].

c) Deposition:

The FIB can also be used to deposit material (platinum or carbon) on different surfaces. Deposit materials are supplied by gas injection system (GIS) that contains the chemical gas compound which is the precursor form and consists of organometallic molecules. When this compound is exposed to the region of interest, beams decompose the molecules locally and deposit highly pure material onto the surface. Platinum and carbon coatings reduce the curtaining effect and allow automatic beam tuning and slice-thickness control [14].

d) Preparation of TEM samples:

Ultramicrotomy with a thin diamond blade which is used for preparation of the thin sections for TEM has several limitations such as: non-uniform slice thickness, inability to choose specific sites of interest, and difficulty when hard or brittle materials such as dental enamel, ceramics and dental composites are used. FIB milling as an alternative milling method works by ablation of a small amount of material when a primary ion beam hits the sample surface with precision milling down to a nanoscale. However, FIB may cause local heat production along the beam path that could alter or damage the sample. The beam damage could be minimized if the thinning is conducted under cryogenic conditions [15].

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