Materials Science and Engineering C 33 (2013) 1455–1459

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Anelastic phenomena associated to water loss and collagen degradation in human dentin

S. Amadori [a,*], E. Bonetti [a], E.G. Campari [a], I. Cappelloni [b], R. Montanari [b]

[a] Department of Physics and Astronomy, University of Bologna, Viale Berti Pichat 6/2, 40127 Bologna, Italy
[b] Department of Industrial Engineering, University of Rome—Tor Vergata, Via del Politecnico 1, 00133 Rome, Italy

ARTICLE INFO

Article history:
Received 3 July 2012
Received in revised form 4 December 2012
Accepted 14 December 2012
Available online 23 December 2012

Keywords:
Dentin
Collagen
Internal friction
Dynamic modulus

ABSTRACT

This work describes the anelastic and dynamic Young modulus behaviour of human dentin from room temperature up to 673 K. Human molars, extracted from individuals (males 55–70 years old) as part of their dental treatment, were cut to obtain bar-shaped samples subsequently used for mechanical spectroscopy experiments. In addition, thermo-gravimetric analysis (TGA) has been performed to assess a possible weight loss occurring in the same temperature range of mechanical spectroscopy tests.

A broad and asymmetric internal friction (Q^{-1}) maximum at 500 K has been observed during the heating of the as-prepared samples. This maximum is absent during the following cooling down to room temperature. It is therefore due to the occurrence of an irreversible transformation in the sample. TGA shows a remarkable weight loss in the same temperature range. This effect has been related to loss of fluids and degradation of collagen.

Another set of samples, previously kept for 36 h under a vacuum of 10^{-2} Pa, were submitted at room temperature to test at increasing strain from 6×10^{-6} to 7×10^{-4}. The results show transient and fully recoverable Q^{-1} increase and dynamic modulus (E) decrease.

The phenomenon has been ascribed to the breaking of weak H-bonds between polypeptide chains forming the triple-helix with consequent increase of the mean length of vibrating chain segments.

1. Introduction

Dentin is a complex hydrated biological composite consisting of about 50 vol.% mineral in the form of apatite, 30 vol.% organic matter, which is largely type I collagen, and about 20 vol.% fluid. Other non-collagenous proteins and organic components are also present in small amounts [1].

Its hierarchical structure is shown in Fig. 1, taken from [2]. For simplicity dentin will be described here by distinguishing three scales (macro, meso, nano) where in some texts more hierarchical levels are defined.

On a macro scale (a–b) dentin can be modelled as a continuous fibre-reinforced composite, with the intertubular dentin forming the matrix and the tubule lumens with their associated cuffs of peritubular dentin forming the cylindrical fibre reinforcement [3–7]. The morphology varies with location since tubules converge on the pulp chamber varying density and orientation.

On a meso scale intertubular dentin is formed by fibres randomly oriented in a plane perpendicular to the direction of dentin formation (c–d–e).

On a nanoscale the characteristic features are collagen fibrils, apatite crystals and water (f–g). Each fibre consists of several fibrils (50–100 nm in diameter) which exhibit periodically spaced gaps. Three polypeptide chains are wound together in a triple helix. A triple-helical molecule is cylindrically shaped (diameter of ~1.5 nm, length of ~300 nm). The molecules are all parallel, but their ends are separated by holes of about 35 nm, they pack together to form a single fibril.

The mineral is either within the fibrils (intrafibrillar) or between the fibrils (interfibrillar). The shape of apatite crystals is needle-like near the pulp and progressively becomes plate-like near the enamel, the thickness, ~5 nm, does not change with location.

Water is the third major component and is located within and between the fibrils, between fibres and between triple-helical molecules.

Several works exist in the literature regarding the mechanical properties of dentin, e.g. [8–11]; a thorough review was published by Kinney and Marshall [8]. The Young's modulus measured by different research groups spans from about 11 GPa up to 35 GPa. In general, static mechanical tests give lower values than the dynamic (particularly ultrasound) ones. Apart from artifacts, like damaged teeth, affecting the tests, it is not completely clear why there is such a spread between different measurements. The probable source for such a wide range of measured values is the anelastic behaviour of dentin. When a material exhibits such a property, its elastic constants are time dependent and different values of Young's modulus can be obtained with different techniques. In particular, static tests yield relaxed values (lower) whereas dynamic

* Corresponding author. Tel.: +39 0512095298; fax: +39 0512095113.
E-mail address: stefano.amadori4@unibo.it (S. Amadori).

0928-4931/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.msec.2012.12.067

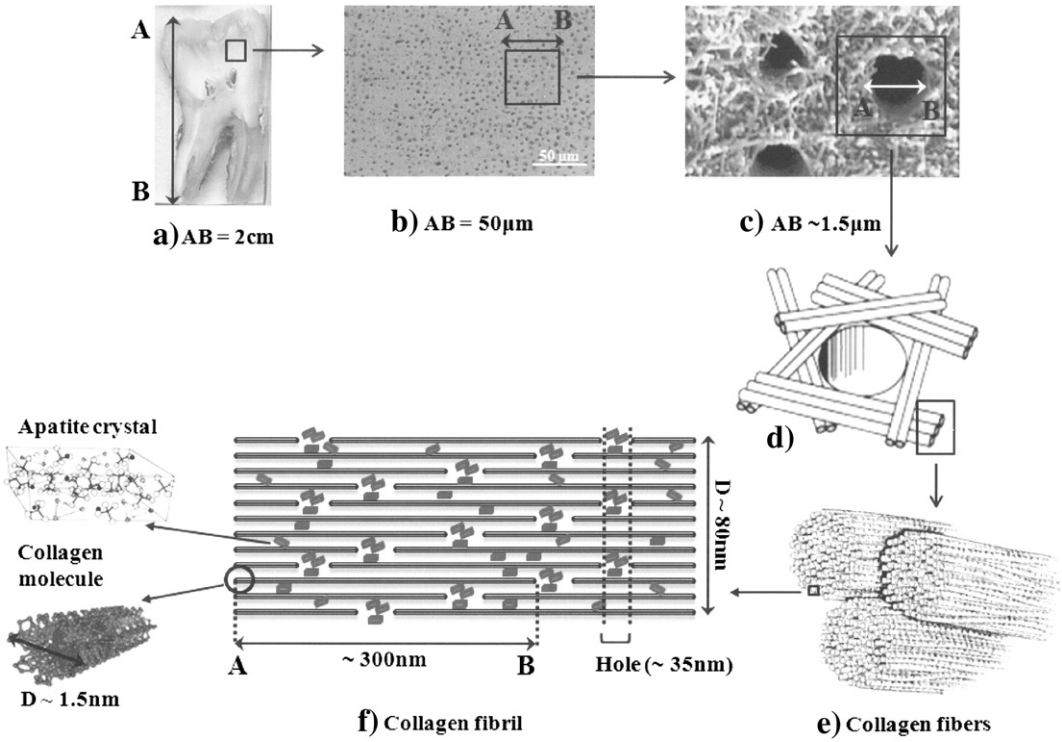

Fig. 1. Schematic view of the highly hierarchical dentin structure [2].

tests yield unrelaxed values (higher). In spite of the importance of the topic, only few papers deal with the anelastic properties of dentin and their changes [12,13]. Therefore, an experimental campaign has been undertaken by the authors to study the anelastic behaviour of dentin under different physical conditions aiming to get ground information.

The aim of this work is to add information on damping phenomena occurring in the range from room temperature up to 673 K. Although clinically relevant temperatures are between 273 and 323 K and temperatures above 500 K are rarely of interest also for the implantation of biomaterials, the anelastic behaviour of dentin has been investigated in a more extended range (up to 673 K) to get ground information about all the possible transformations of its complex structure induced by heating, including the complete degradation and combustion of collagen. For instance, such information could be useful in the study of archaeological finds or in forensic cases.

2. Experimental

Human molars were extracted from individuals (males 55–70 years old) as part of their dental treatment. The teeth were not identified by patient number or name and each patient signed a patient consent form. After disinfection by immersion in a solution of sodium hypochlorite in water for about 12 h, they were sectioned along mesial direction by using a precision diamond saw with water cooling in order to obtain 0.8 mm-thick slices. From these sections bar-shaped samples (length $L = 13 \div 16$ mm, width $W = 3 \div 4$ mm) have been cut for mechanical spectroscopy measurements. A single specimen was obtained from each tooth and included root dentin and crown dentin but not enamel. Teeth taken from different patients (sixty patients, one tooth per patient) have been used in the experiments. Before testing the specimens have been investigated by scanning electron microscopy and light optical microscopy and one third of the samples was rejected because of the presence of fractures or damages.

The samples, mounted in free-clamped mode, have been tested by the vibrating reed technique in a vacuum chamber at a pressure of 10^{-2} Pa. The vibrating reed analyzer model VRA 1604 by CANTIL srl was employed. The apparatus is described in detail in [14]. Young's modulus and damping were measured. The damping Q^{-1} which is also the ratio of the loss modulus to the storage modulus was determined from the logarithmic decay δ of flexural vibrations:

$$\tan\delta = \left(E''/E'\right) = \ln\left(A_n/A_{n+1}\right) = \pi Q^{-1} \tag{1}$$

where A_n and A_{n+1} are the amplitude of two successive vibrations, E' and E'' are the storage and loss modulus respectively.

The storage modulus (also called elastic modulus) has been determined from the resonant frequency f of the bar samples:

$$E = \left[48\pi^2\rho l^4/\alpha^4 h^2\right] f^2 \tag{2}$$

α is a constant, ρ is the material density, l and h are the sample length and thickness, respectively.

The strain amplitude was kept below 1×10^{-5}, and the vibration frequency of the samples spans the 1–10 kHz frequency range.

A first set of measurements consisted of heating–cooling cycles from 300 to 673 K with a constant heating rate of 3.33×10^{-2} K s^{-1}.

A second set of measurements was carried out isothermally at 300 K with increasing strain amplitudes. Fifteen specimens were used for each set of tests. In the second set of measurements before starting the isotherms, specimens were kept for 1.3×10^5 s (about 36 h) in the spectrometer chamber at room temperature at the pressure of measurements of 10^{-2} Pa. These samples were submitted to a strain increase from 6×10^{-6} to 7×10^{-4}, then kept at the maximum strain for 1.2×10^3 s (20 min) and finally brought back to the initial condition. Successive measurement runs were made on the same samples.

Thermo-gravimetric analysis (TGA) has been performed from room temperature up to 693 K on ten samples submitted to the same heating runs employed in mechanical spectroscopy experiments to assess a possible weight loss.