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ORIGINAL ARTICLE

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Nanohybrid scratch resistant coatings for teeth and bone viscoelasticity manifested in tribology

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Abstract We cover teeth surfaces with nanohybrid coatings containing an inorganic ceramic and an organic copolymer constituents. We report the first ever values of scratch penetration depth and scratch recovery for bare and coated teeth. We find that uncoated teeth undergo viscoelastic recovery (healing) after microscratching – the first manifestation of bone viscoelasticity in tribology. The coatings fill "valleys" in teeth surfaces. In each case a large improvement in the scratch resistance as compared to uncoated teeth is seen. The extent of the improvement depends on the inorganic/organic component ratios in the nanohybrids.

Keywords Nanohybrids · Inorganic + organic materials · Viscoelasticity in tribology · Teeth coatings · Bone viscoelasticity

Introduction and scope

Nearly 95% of the whole human population suffers or has suffered at some stage of their lives from tooth decay or some other disease related to the oral environment [1]. At the same time, biomaterials pose certain fundamental scientific questions related to surprising properties of calcified tissue. Indeed, the ability of the bone to recover from damage as well as its mechanical toughness are under discussion [2, 3, 4, 5, 6]. The effect of the mineral phase crystallites, which are known to be responsible for stiffness of the bones cannot account for the ability of the bones to withstand mechanical impacts. Bone is a nanocomposite of hydroxyapatite and an organic matrix, with collagen as the main component of the latter. On the basis of atomic force microscopy indentation testing, Thompson and coworkers [2] have postulated the existence of sacrificial bonds in collagen, which undergo scission under an external force but reform when the force is removed. Their results seem supported by those of Smith and coworkers [7] for abalone nacre. However, other models exist also [4, 5] and Currey [3] states that "there is still a considerable element of speculation in all this." Our results reported below show that bones exhibit *viscoelasticity in tribological testing* – similarly as polymeric materials do [8]. This is in clear contrast to metals, which show elastic and plastic behavior only, and ceramics, which are elastic only and this in a narrow range of applied stresses [9]. Our findings should also be contrasted with the existing methods of study of viscoelasticity, namely by dynamic mechanical analysis (DMA) as discussed in detail by Menard [10] and by dielectric spectroscopy explained by Gedde [11]. In DMA one determines

$$\tan \partial = E''/E' \qquad (1)$$

as a function of either temperature T or frequency ω of imposed sinusoidal oscillations. Here E' is the storage modulus representing elastic (solid-like) behavior and E'' is the loss modulus representing viscous flow (liquid-like) behavior. All mechanical quantities featured in Eq. (1) have their analogs in dielectric measurements.

The study of materials surfaces – tribology – is well developed for metals [12] but much less for other classes of materials. Thus, no reports have been found in the

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literature related to the tribological properties of human teeth – with or without coatings. In fact, the wear behavior of calcified tissue has received very limited attention due, among other things, the lack of proper experimental procedures for measuring these characteristics in bones and teeth [4].

Basing on the pioneering work of Roy on sol-gel process [13, 14], we have developed methods of preparing hydroxyapatite with controlled structures [15, 16, 17]. This plus our work on polymeric materials [18, 19, 20, 21] has led us to nanohybrids, which are neither inorganic nor organic but a nanoscale combination of both [22]. The existing situation and the knowledge already accumulated have behooved us to define the following set of objectives for this work: development of a methodology for the determination of scratch resistance of uncoated or coated human teeth; determination of teeth behavior under scratching; application of nanohybrid materials [22] or development of new ones as teeth coatings; and comparison of the scratch resistance of bare and coated teeth.

Systems studied

Our nanohybrid coatings are vastly different from in situ ceramic coatings deposited on ceramics and developed by Ishikawa and coworkers [23]. While polymeric constituents participate in their process, their final product is not a hybrid but a ceramic only. Our nanohybrids are also different from nanocomposite hydrogels of Haraguchi and Takehisa [24]. Their composites undergo swelling while our nanohybrids do not. While in certain cases such as electroplating of inorganic glass *roughening of the surface* is required to achieve adhesion [25], it is not needed for our coatings. Our nanohybrids are also much different from *heterogeneous composites* [26] such as graphite + epoxy laminates [27] in which the units of the reinforcing component are so large that they might be visible with a naked eye.

We create a copolymer containing poly(methyl methacrylate) sequences by free radical polymerization in the presence of a polymerization initiator. Commercial ceramic nanoparticles 15–18 nm in diameter are functionalized and then slowly mixed with the copolymer. Conventional mixing is sufficient, while sophisticated techniques such as sintering of compacted polymer-based materials [28] are of course available. Details will be provided elsewhere, but fairly strong interactions between the inorganic and the organic constituents are needed for the formation of the nanohybrid [22]. We have thus created a series of four coatings with varying contents of ceramic nanoparticles, namely with 12, 20, 25, and 30 wt% of the ceramic.

Non-erupted molar teeth were extracted from several volunteers and cut into 4 pieces each with a diamond disc, washed with distilled water and dried. The pieces were etched with 37% phosphoric acid dental grade (Degufill) for 15 s and then washed with distilled water and dried.

Scratch testing

We have decided to determine tribological – here scratch sensitivity – behavior of teeth adopting a methodology used before for polymer surfaces [8]. The measurements were carried with a Micro-Scratch-Tester of CSEM Instruments at the constant load of 5 N, the groove length=2 mm and a 200 μm radius diamond tip. The accuracy according to CSEM is ±7.5 nm, much more than needed since the depths we measure are of the order of microns. We have also determined the viscoelastic recovery (healing, residual depth) under the load of 0.03 N. A schematic of this machine is provided in [29] while other experimental details are given in [8].

Results for uncoated teeth: viscoelasticity in tribology

Figures 1 through 3 show the tribological behavior of a bare tooth (Fig. 1), a tooth covered with the nanohybrid coating containing 12 wt% ceramic (Fig. 2) and of a tooth +25% ceramic coating (Fig. 3). For each class (including the other ceramic concentrations named above), we have studied four teeth and performed 18 experiments for each tooth. The results for the same tooth, with the same coating (or without coating), obtained at different locations are different, thus averaging would not make sense. In simple hardness experiments such as those of Rockwell

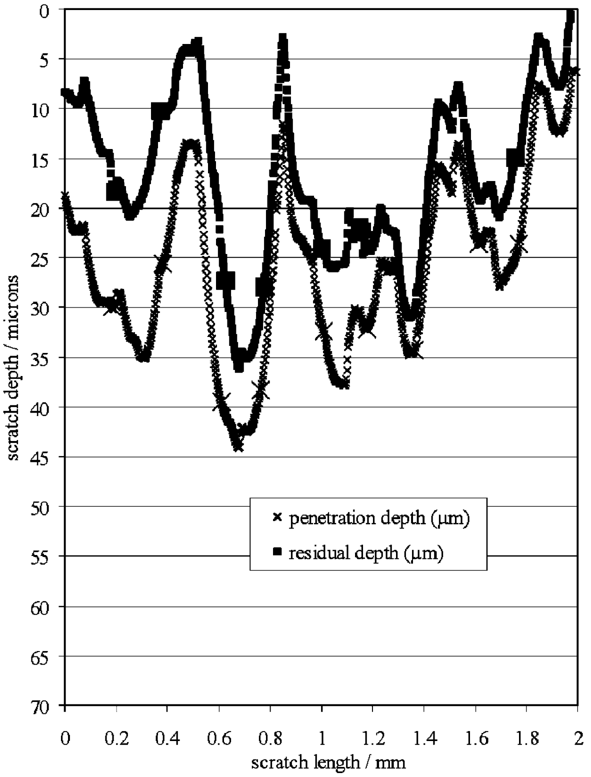

Fig. 1 Tribological characteristics of a microscratch along an uncoated tooth. The difference between the penetration depth R_p and the recovery depth R_h constitutes the viscoelastic healing

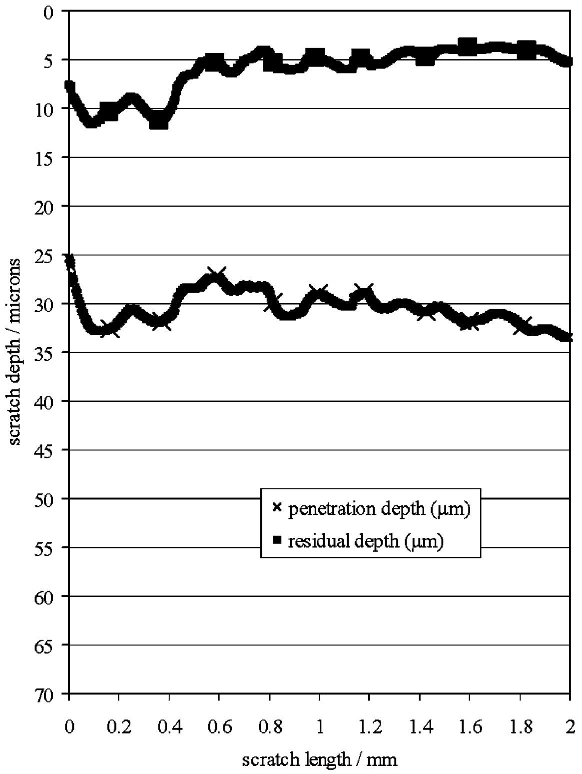

Fig. 2 Tribological characteristics of a microscratch along a tooth with nanohybrid coating containing 12 wt% of ceramic nanoparticles. The curves are anologous to those in Fig. 1

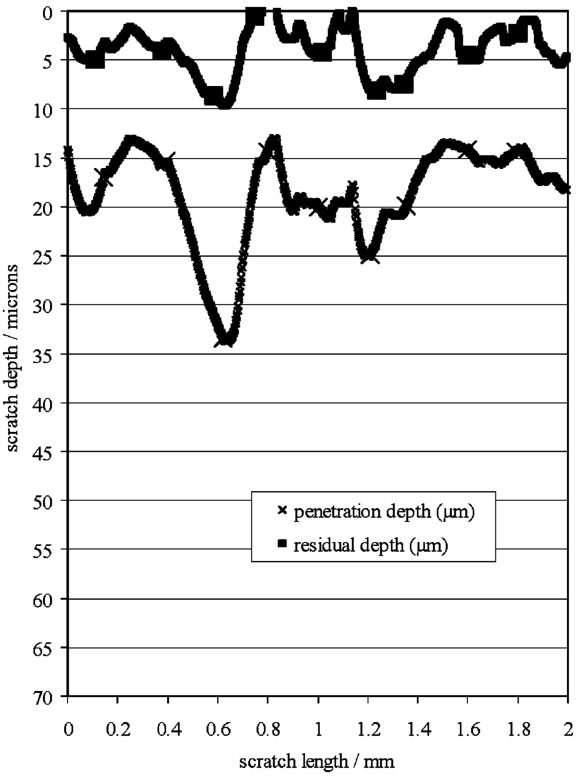

Fig. 3 Tribological characteristics of a microscratch along a tooth with nanohybrid coating containing 25 wt% of ceramic nanoparticles. The curves are anologous to those in Fig. 1

hardness, one often assumes that the tribological properties are the same at every point of the surface. Our results show how *totally inapplicable* is this assumption to teeth surfaces – while our apparatus allows mapping of uneven surfaces such as those of the teeth.

Each figure contains the plots of the original penetration depth R_p and of the recovery depth R_h after 5 min. Actually 3 min are sufficient for the recovery; strongly viscoelastic behavior is seen in bare teeth as well as in teeth covered with the nanohybrids. We show R_p and R_h values as a function of the location along the moving diamond tip up to 2 mm.

For brevity we include here results for one uncoated tooth; the results for other bare teeth are similar. Consider now the results in Fig. 1. We see that *there is viscoelastic recovery* (*healing*). This is the case also for all other nude teeth we have investigated. By definition, viscoelasticity involves changes of mechanical properties with time [9, 10, 11, 18, 20, 30, 31, 32, 33, 34, 35]. If there were no recovery at all, the curves of the penetration depth and the recovery depth would simply coincide. If there were purely elastic recovery, the differences between the two curves would be much smaller; a tooth cannot be elastically deformed as much as a steel spring can.

The prevailing method of determination of viscoelasticity is dynamic mechanical testing [10] – as represented above by Eq. (1). As briefly mentioned in the Introduction, the dielectric method can be also used for the purpose [11] although it is much less popular. DMA is classified as a part of Mechanics – for good reasons. J. Vincent discusses in detail the basic tenets of the theory of viscoelasticity and its application to mechanics of structural biomaterials [31]. Currey briefly echoes the fact that the mechanical behavior of bones is viscoelastic [33]. However, Tribology is considered as a field separate from Mechanics [12, 36]. The results displayed in Fig. 1 show that the viscoelasticity of bones manifests itself also in Tribology, namely in scratch healing.

Tschoegl has argued that “In principle, however, all real materials are viscoelastic” (p. 35 in [30]). Needless to say, the viscoelasticity of ceramics – for instance – can be neglected for all practical purposes [9]. Following Tschoegl’s argument, however, let us go back to results from our laboratory for materials known to be viscoelastic, namely a commercial epoxy + a thermoplastic additive of varying concentration [8]. We have defined then the percentage recovery in scratch testing as

$$\phi = (1 - R_h/R_p)100\% \qquad (2)$$

where R_h and R_p have been defined above. The results reported in [8] show the percentage recovery ϕ values ranging from 55–95% or so. The systems studied in [8] are "purely" viscoelastic. Since bones contain hydroxyapatite, it was not certain in advance whether the bone viscoelasticity will appear in a pronounced way in scratch testing. Antich and coworkers have shown [37] using ultrasound critical angle reflectometry (UCR) that the bone behavior is affected by subtle changes in the organic matrix. UCR developed by Antich [38, 39] is a sensitive and convenient technique enabling sample rotation, an advantage we have used in determination of orientation induced by a magnetic field in a longitudinal polymer liquid crystal [40]. However, the results in Fig. 1 show that the viscoelastic recovery is quite pronounced. Thus, we find a common feature of the bone and polymeric materials: viscoelasticity manifests itself in scratch healing in both classes of materials.

The theory of bone recovery of Thompson and coworkers [2] mentioned in the beginning is in fact a viscoelastic theory. Our results shown in Fig. 1 agree with their model: the recovery we observe can be explained in terms of bond reforming after the force imposed on the surface by the scratching diamond is removed. In their case the force was applied by indentation and in our case by an object moving along the surface but the response of the material is similar in both cases.

Results for coated teeth

For brevity we do not include here results for teeth coated with 20 and 30% of the ceramic, for other uncoated teeth, nor for other teeth with 12% and 25% of the ceramic.

In Fig. 2 we show results for a tooth with a nanohybrid coating containing 12% of ceramic nanoparticles. The first and striking result is that both the penetration curve and the residual curve are *shallower* than the respective curves for the uncoated tooth in Fig. 1. Thus, an important practical objective has been achieved: the nanohybrids coating we have developed provide significant protection against scratching. As stated previously, the matrix of our nanohybrid material is poly(methyl methacrylate). Goldman [41] has demonstrated how in polymers viscoelastic recovery consists of short-range motions as well as long range motions that involve entanglements and/or networks.

Wear can be defined as the unwanted loss of solid material from sliding surfaces due to mechanical interaction [9, 12, 29]. We have defined a quantitative measure of wear in terms of multiple scratching results [42]. Thus, our coatings – their viscoelastic recovery in particular – should also diminish wear or detrimental changes to the tooth surface caused by multiple scratching.

The second significant difference between Figs. 1 and 2 is the fact that the uncoated tooth in Fig. 1 shows much larger vertical distances between consecutive minima and maxima. We have also performed for each tooth a *topography determination* by using the constant load of 0.03 N, this before applying the scratching load of 5 N. The topography determinations confirm the results shown in the Figures: the coating fills the "valleys" in the tooth, diminishing the vertical distances between bottoms of the "valleys" and "top ridges" on the tooth surface. Thus, our nanohybrid coatings perform a dual role: protection of the teeth against scratching and wear and at the same time smoothing the natural generally irregular teeth surfaces.

In Fig. 3 we have a region centered approximately around the 0.6 mm location along the horizontal axis where both the penetration depth and the recovery depth have higher values than elsewhere on the same tooth. This only confirms the fact noted already about the irregularity of tooth surfaces; there is an unusually deep "valley" on the tooth surface at this particular location. If we put this region aside, we see that the penetration depth oscillates around 30 μm in Fig. 2 and around 20 μm in Fig. 3. Similarly, the recovery depth oscillates around 7 or 8 μm in Fig. 2 and around 5 μm in Fig. 3, sometimes even reaching practically 0. Thus, approximately doubling the contents of the ceramic nanoparticles (from 12–25 wt%) provides also a stronger coating which better resists scratching.

We find that both the original penetration depth and the recovery of the surface are functions of the ratio of the ceramic nanoparticles to the polymer in the coatings. Indeed, as seen in all figures, the recovery of the teeth surface after 5 min changes significantly with the material composition. Thus, the coatings not only improve the scratch resistance of the teeth but also induce a *shape memory effect* of interest for both fundamental understanding and application purposes.

Concluding remarks

While J. Vincent discusses the viscoelasticity of bones as manifested in mechanics [31], viscoelasticity does not seem to be yet in the mainstream of biomedical engineering. A textbook of that discipline by Dee, Puleo and Bizios [43] does not include the word "viscoelasicity" in it subject index; the same applies to the word "tribology". Progress in the application of the time-temperature correspondence [18, 20] and the time-stress correspondence [19, 21] has not yet extended to biomaterials – where the 1955 so-called WLF equation [31] is still in use.

Vincent does discuss important results of Lakes and Katz [44] who have assigned several relaxational processes in the bone to distinct structural elements. Lakes and Katz see the relaxations in the values of tan ∂ as a function of the frequency ω of sinusoidal oscillations at a constant temperature; see again Eq. (1).

We have noted in the beginning the model of Thompson et al. [2] explaining the bone viscoelasticity in terms of re-formation of sacrificial bonds, and the results of Smith et al. [7] for abalone nacre which seem to support the model. Our direct demonstration of the bone viscoelasicity in tribology reported above agrees also with the model of Thomson and coworkers. The totality of these results seems to diminish significantly the "speculation" noted by Currey [3].

Our fundamental results are combined with a practical one: we have demonstrated the feasibility of producing scratch-resistant coatings for teeth on the basis of nanoengineered hybrid materials. There exists a clear relation between the contents of the inorganic phase (i.e. the nanoparticles of the ceramic) and the tribological response of the coating. We note the possibility of tailoring surface properties of our nanohybrids by controlling the chemistry of the coating, depending on the particular application. Clinical studies in animals and humans are being carried out to rule out any potential hazards from our coatings; these results will be reported separately.

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References

1. Saenz A, Brostow W, Castaño VM (1999) J Mater Ed 21: 281
2. Thompson JB et al. (2001) Nature 414: 773
3. Currey J (2001) Nature 414: 699
4. Oliver WC, Pharr GM (1992) J Mater Res 7: 1564
5. Zioupos P, Currey JD (1994) J Mater Sci 29: 978
6. Vashishth D, Tanner KE, Bonfield WJ (2000) J Biomech 33: 1169
7. Smith BL et al. (1999) Nature 399: 761
8. Brostow W, Bujard B, Cassidy PE, Hagg HE, Montemartini P (2002) Mater Res Innovat 6: 7
9. Brostow W (1979) Science of Materials. Wiley, New York; Robert E. Krieger (1985), Malabar, FL; Brostow W (1985) Introducción a la ciencia de los materiales, Limusa, Mexico, DF; Brostow W (1985) Einstieg in die moderne Werkstoffwissenschaft, Hanser, München
10. Menard KP (1999) Dynamic Mechanical Analysis. CRC Press, Boca Raton
11. Gedde UW (1995) Polymer Physics, Kluver, Dordrecht
12. Rabinowicz E (1995) Friction and Wear of Materials, 2nd edn. Wiley, New York
13. Roy R (1974) Nature 247: 25
14. Roy R (1987) Science 238: 1664
15. Rivera EM et al. (1999) Mater Lett 41: 128
16. Rivera-Muñoz E, Diaz JR, Rodriguez JR, Brostow W, Castaño VM (2001) J Mater Sci Med 12: 305
17. Riviera-Muñoz E, Brostow W, Rodriguez R, Castaño V M (2001) Mater Res Innovat 4: 222
18. Brostow W, Corneliussen RD (eds) (1986) Failure of Plastics. Hanser, Munich
19. Brostow W (2000) Mater Res Innovat 3: 347
20. Brostow W (ed) (2000) Performance of Plastics. Hanser, Munich
21. Akinay AE, Brostow W, Castaño VM, Maksimov R, Olszynski P (2002) Polymer 43: 3593
22. Brostow W, Castaño VM, Huanosta A, de Icaza M, Nicho ME, Saniger JM (1999) Mater Res Innovat 3: 85
23. Ishikawa T et al. (2002) Nature 416: 64
24. Haraguchi K, Takehisa T (2002) Adv Mater 14: 1120
25. Schammler G, Springer J (1995) J Adhesion Sci Technol 9: 1307
26. Brostow W et al. (1998) Polymer Eng & Sci 28: 785
27. Binienda WK, Reddy ES (1992) J Reinf Plastics & Composites 11: 324
28. Narkis M (1995) In Narkis M, Rosenzweig N (eds) Polymer Powder Technology Ch 10. Wiley, Chichester, p 279
29. Brostow W, Deborde J-L, Jaklewicz M, Olszynski P (2003) J Mater Ed (submitted)
30. Tschoegl NW (1989) The Phenomenological Theory of Linear Viscoelastic Behavior. Springer, Berlin Heidelberg New York
31. Vincent J (1990) Structural Biomaterials. Princeton University Press, Princeton
32. Michler GH (1992) Kunststoff-Mikromechanik. Hanser, München
33. Currey J (1994) The Mechanical Adaptation of Bones. Princeton University Press, Princeton
34. Goldman AY (1994) Prediction of Deformation Properties of Polymeric and Composite Materials. American Chemical Society, Washington, DC
35. Mark JE (ed) (1996) Physical Properties of Polymers Handbook. American Institute of Physics Press, Woodbury, NY
36. Zambelli G, Vincent L (eds) (1998) Matériaux et contacts – Une approche tribologique. Presses polytechniques et universitaires romandes, Lausanne
37. Mehta SS, Öz OK, Antich PP (1998) J Bone Min Res 13: 114
38. Antich PP et al. (1991) J Bone Min Res 6: 417
39. Mehta P, Antich S, Landis W (1999) Conn Tissue Res 40: 189
40. Brostow W, Jaklewicz M, Mehta S, Montemartini P (2002) Mater Res Innovat 5: 261
41. Goldman AY (2003) 11-th Annual POLYCHAR World Forum on Advanced Materials. University of North Texas, January 6–10
42. Brostow W, Damarla G, Howe JA, Pietkiewicz D (2003) 11-th Annual POLYCHAR World Forum on Advanced Materials. University of North Texas, January 6–10
43. Dee KC, Puleo DA, Bizios R (2002) An Introduction to Tissue–Biomaterial Interactions. Wiley, Hoboken NJ
44. Lakes RS, Katz JL (1979) J Biomech 12: 679