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Research Paper

Nanomechanical responses of human hair

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ABSTRACT

Here we report the first ever studies on nanomechanical properties e.g., nanohardness and Young's modulus for *human hair of Indian origin*. Three types of hair samples e.g., virgin hair samples (VH), bleached hair samples (BH) and Fe-tannin complex colour treated hair samples (FT) with the treatment by a proprietary hair care product are used in the present work. The proprietary hair care product involves a Fe-salt based formulation. The hair samples are characterized by optical microscopy, atomic force microscopy, field emission scanning electron microscopy, energy dispersive X-ray spectroscopy (EDAX) genesis line map, EDAX spot mapping, nanoindentation, tensile fracture, and X-ray diffraction techniques. The nanoindentation studies are conducted on the cross-sections of the VH, BH and FT hair samples. The results prove that the nanomechanical properties e.g., nanohardness and Young's modulus are sensitive to measurement location e.g., cortex or medulla and presence or absence of the chemical treatment. Additional results obtained from the tensile fracture experiments establish that the trends reflected from the evaluations of the nanomechanical properties are general enough to hold good. Based on these observations a schematic model is developed. The model explains the present results in a qualitative yet satisfactory manner.

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Introduction

Human hair is a cylindrically concentric polymeric nanocomposite biological fibre (Harland et al., 2014). It bears a unique hierarchical functionally graded microstructure (FGM) along the cross section (Liu et al., 2014). For instance, the simplest or smallest component of hair is nanofibril of dimension as low as 3–5 nm (Matsunaga et al., 2013) while the human hair is about 50–100 μm in diameter and nearly 50–300 cm in length (Vargiolu et al., 2013). This is such a unique natural structure that anything similar is yet to be developed as a man-made composite. If at all developed, such a synthetic composite needs to have microstructural unit spanning the range of as small as a nanometre to as big as more than a metre. This unique structure works as the basic challenge to the mechanics and mechanism research communities as well as to materials science research community (Harland et al., 2014; Liu et al., 2014; Matsunaga et al., 2013; Vargiolu et al., 2013; Dario et al., 2013; Estibalitz et al., 2012; Tohmyoh et al., 2011; Jamart et al., 2015; Fang and Koppl, 2015; Bruce et al., 2015). The call of the moment is, of course, the development of better understanding about the nano and microstructure of hair components and corresponding mechanical properties (Harland et al., 2014; Liu et al., 2014; Matsunaga et al., 2013; Vargiolu et al., 2013) as well as the development of environmentally more benign, less toxic hair care products (Dario et al., 2013; Estibalitz et al., 2012).

All hair macrofibrils are now known to possess a similar (e.g., ~0.4) polymer matrix fraction (Harland et al., 2014). These are typically composed of a doubly-twisted architecture. In this design a central intermediate filament (IF) is surrounded by concentric rings of tangentially-angled IFs (Harland et al., 2014). The high sulphur (HS) keratin associated proteins (KAPs) and the ultra high sulphur (UHS) KAPs provide the cross-linking ability in the disulphide bond that in turn provides the mechanical strength in human hair (Liu et al., 2014). The glycine-tyrosine (HGT) KAPs also contribute to the mechanical robustness of hair (Matsunaga et al., 2013). But three-point bend strength at failure does not correlate with the surface morphology of cuticles present on the hair surface (Vargiolu et al., 2013). Due to localized degradations of KAPs, melanin pigments and lipids marked deterioration in mechanical properties of human hair happens on exposure to ultraviolet rays (Dario et al., 2013; Estibalitz et al., 2012). The Young's modulus and yield stress of beard hair are significantly affected by the presence of moisture. However, the effect of strain rate variation on these properties is not so significant (Tohmyoh et al., 2011).

The macrostructure of human hair typically comprises of micro and sub-microstructural elements such as the "α" helix (diameter-10 Å), the cuticles (0.3–5 μm), cuticle cells (5–10 nm) and about 5–10 scales thick cuticle layer (Bhushan and Chen, 2006; Danforth, 1939; Garn, 1947; Lodge and Bhushan, 2006; Robbins, 1994). Cross section of healthy hair comprises of the most dense medulla region surrounded by a denser cortex region surrounded by the cuticular region of roof tile architecture (Bhushan and Chen, 2006; Danforth, 1939; Garn, 1947; Lodge and Bhushan, 2006; Robbins, 1994; Thibaut et al.2007). The cross section is circular for straight hair samples. It is elliptical for curly hair samples from the scalp and beards (Danforth, 1939; Garn, 1947; Thibaut et al.2007; Xu and Chen, 2011).

For cylindrically concentric polymeric nanocomposite biological fibre with a unique FGM such as the human hair the knowledge of structure-property correlation is of extraordinary academic significance. Apart from pure academic significance, from material science point of view as well such strategic knowledgebase bears extraordinary scientific and technological importance (Lodge and Bhushan, 2006).

In spite of such strategic importance for microstructurally tuned, engineered material design, however; the total amount of research reported on macromechanical, nanomechanical, and nanotribological properties of human hair in general, and human hair of *Indian* origin in particular; is far from significant (Thozur et al., 2006; Maxwell and Huson, 2005; Bhushan et al., 2005; Cliffor et al., 2005; LaTorre and Bhushan, 2005; Seshadri and Bhushan, 2008; Smith and Swift, 2002). This backdrop is one of the main motivations for carrying out the present work.

The macromechanical properties e.g., tensile failure strength, yield stress, failure strain, as well as nanomechanical properties e.g., nanohardness and Young's modulus of human hair are sensitive to humidity (Thozur et al., 2006; Maxwell and Huson, 2005), ethnic origin and condition of the hair e.g., whether virgin, hair conditioner treated, mechanically and/or chemically damaged (Bhushan et al., 2005; Cliffor et al., 2005; LaTorre and Bhushan, 2005). Tensile response of human hair also depends on morphology (Seshadri and Bhushan, 2008). The typical scatter in nano-and-macromechanical properties of hair is generally very high i.e., about 20–30% (Bhushan et al., 2005; Cliffor et al., 2005; LaTorre and Bhushan, 2005; Smith and Swift, 2002).

The binding interaction between the colouring element in a hair-care product and the hair surface/cortex is one of the most important factors that modify the physical and mechanical properties of hair (Chen and Bhushan, 2006). Due to localized softness created by conditioner treatment, the effective Young's modulus of human hair drops even by almost an order of magnitude e.g., from $\sim 5.4 \pm 0.9$ to 0.61 ± 0.03 GPa respectively, for virgin- and conditioner treated hair surfaces in correspondence (Smith and Swift, 2002). In addition, hair friction is strongly sensitive to humidity and temperature (Bhushan et al., 2005).

At present the permanent hair colour market is dominated by the p-PDA (Para phenyl diamine) based colour (Chisvert et al., 2007). The use of p-PDA in hair colour is a worldwide concern due to its acute toxicity. However, there are many reports on the toxic effect of p-PDA and p-PDA derivatives based hair colour (Nohynek et al. 2004). Therefore, scientists are trying to develop p-PDA free permanent hair colour. However, despite many efforts widely accepted black and black shades could not be prepared without p-PDA. An alternate approach to solve this problem is utilisation of metal nanoparticle/metal complex/oxide based colouring. Therefore, the interaction of metal with hair is of utmost interest. The physical properties of hair may change upon metal treatment. The deterioration of physical properties upon metal treatment is a major concern. Therefore this