Thermochimica Acta 661 (2018) 78–83

Contents lists available at ScienceDirect

Thermochimica Acta

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

Kinetics of the changes imparted to the main structural components of human hair by thermal treatment

F.J. Wortmann[a,*], G. Wortmann[a], C. Popescu[b,1]

[a] School of Materials, The University of Manchester, Manchester M13 9PL, United Kingdom
[b] DWI—Leibniz-Institute for Interactive Materials, Forckenbeckstrasse 50, D-52056 Aachen, Germany

ARTICLE INFO

Keywords:
Human hair
Thermal treatment
Structural damage
Keratin protein denaturation
DSC

ABSTRACT

Thermal straightening of hair is a wide-spread consumer practice, which will impart specific hair damage. For practically relevant, cumulative conditions of thermal treatment (straightening iron, 200 °C, 100–800 s) untreated and oxidized (bleached) hair were investigated by DSC in water to determine the time-dependent changes of protein denaturation enthalpy (ΔH_D) and temperature (T_D). Assuming the standard two-phase morphology, the parameters are associated in specific ways with the α-helical proteins (ΔH_D) in the intermediate filaments (IF) and their associated matrix (T_D), respectively. Both parameters show systematic decreases with treatment time with synergistic effects of oxidation. The decrease can in all cases be described by a 1st-order type kinetic model. These predict that ΔH_D, and thus the contents of α-helical material in the IFs, will approach zero for longer times of thermal treatment. The half-life time for the process is consistently about 20–25 min. A two-level, 1st-order approach shows that T_D approaches limiting lower values with comparatively short half-times (untreated:~ 5 min, oxidized:~ 1 min). The approaches thus succeed to provide specific kinetic models for the thermal degradation in IFs and matrix, including the synergistic effects of bleaching. The kinetic approaches are expected to be useful in the context of a range of further analytical investigations of thermal hair treatments.

1. Introduction

1.1. Practical context of the study

The well-established practice of treating slightly curly or frizzy European hair with flat, heated 'irons' provides an effective grooming tool to achieve straighter hair.

Due to the relevance of this grooming practice in the market place, the expert working group 'Hair Care Products' of the DGK (Deutsche Gesellschaft fuer Wissenschaftliche und Angewandte Kosmetik e.V.) has been conducting a comprehensive study to contribute to our understanding of the objective as well as subjective changes of European hair through thermal straightening. Part of the study has been an extensive consumer survey.

The study shows that the majority of consumers applies temperature settings on their devices between 150 °C and 190 °C, where there seems to be an acceptable trade-off between styling effects and undesirable hair changes [1,2].

1.2. Structural and molecular basis of non-permanent hair deformation

Human hair, similar to all other α-keratinous fibres, exhibits a complex set of structures from the microscopic down to the molecular level [3]. The two main morphological components on the microscopic scale are the cuticle, as outer protective layers, and the fibre core (cortex). Due to the limited amount of cuticle (approx. 10%) a specific contribution is usually neglected in the context of mechanical and thermal analyses. The cortex, in a first but rather plausible and successful approximation, going back to Feughelman [4], is described as a two-phase, filament/matrix composite.

In this model the intermediate filaments (IFs) or rather their α-helical structures are the filaments and the matrix consists of the IF-associated proteins (IFAPs). Applying the model for the whole fibre, the term 'matrix' is extended to comprise all amorphous fibre components, that is IFAPs as well as the cuticle and other minor components, such as the cell membrane complex. For specific experimental contexts, [5–10] more complex models are necessary for satisfactory data analysis and discussion.

The straightening effects of the heat treatment are primarily due to

* Corresponding author at: School of Materials, University of Manchester, Sackville Street Bldg. C47, Manchester M13 9PL, United Kingdom.
E-mail address: franz.wortmann@manchester.ac.uk (F.J. Wortmann).
[1] Current address: Kao Germany GmbH, Pfungstaedterstrasse 98-100, D-64297 Darmstadt, Germany.

https://doi.org/10.1016/j.tca.2018.01.014
Received 24 November 2017; Received in revised form 17 January 2018; Accepted 19 January 2018
0040-6031/

'cohesive set' relating to the breakage and reformation of hydrogen bonds in the hair proteins [11–14]. The rearranged bond network is reasonably stable until exposure to humid conditions or washing [1,15,16]. This lack of stability is due to the sensitivity of the hydrogen bonds to moisture, as reflected in the humidity dependent glass transition and viscoelastic properties of keratin fibres, such as human hair [13,17–19]. A related practice uses curved heated surfaces to impart more or less pronounced curls to straight hair.

Hair straightening or other heat treatments at moderate or high temperatures may impart extensive changes to the various morphological components of human hair [20–25]. In practice about 190 °C are considered as a viable compromise between the straightening results and hair damage [26,27]. However, in order to achieve faster and longer lasting grooming results, higher temperatures are available in straightening devices [28], which approach (≈210 °C) or even enter (≈230 °C) the range of keratin denaturation and pyrolysis in dry hair [20,29–31].

1.3. Basis of the study and objectives

The material for the study consisted of commercial, brown hair tresses in their natural as well as in strongly oxidized (bleached) form. The tresses were treated with a commercial straightening device set to 200 °C for cumulative times of 100 s, 300 s, and 800 s, respectively. A group consensus had been reached that this would be expected to represent roughly 2, 6, and 16 months of normal grooming practice. The temperature is somewhat above the usual practical range, but still well below the pyrolysis range [20,29–31] and was chosen to increase the probability that effects would in fact be detectable, while avoiding the excessive temperature range (up to 230 °C).

Though effects of cohesive set, being related to the humidity-dependent glass transition of hair [19] are expected to be fully reversible, it is nevertheless expected that practical relevant heat treatments of human hair, namely with repeated use, will impart a variety of substantial, cumulative and irreversible changes to human hair.

Here we report investigations of untreated and oxidized hair samples by Differential Scanning Calorimetry (DSC) in water. This method specifically enables to assess changes of the thermal stability of the main morphological components in the two-component composite structure of the cortex of hair [4], namely, of the helical proteins in the IFs and of the amorphous matrix [32–34].

The objective is to develop generally applicable approaches to model the time-dependence of the parameter changes for a representative treatment temperature. These will be linked to changes of the thermal stability of IFs and IFAPs and will furthermore enable the assessment of the synergism of the oxidative pre-treatment.

2. Materials and methods

2.1. Hair material

Commercial, Caucasian mixed hair, untreated, medium brown (Kerling, Backnang, Germany) was used for the investigations, in what follows referred to as 'natural'. The hair was in the form of tresses (19 cm long, 1.5 cm wide). An overall number of 12 tresses was split into two groups. The first group was left chemically untreated, while the second group was subjected to a bleaching process twice (bleached).

2.2. Chemical treatment

The bleaching process (hair oxidation) was performed by applying a commercial product (Wella, Darmstadt, Germany) based on an alkaline solution (pH 10.5) of hydrogen peroxide (9%) and ammonium persulfate, applied for 30 min and at room temperature. This treatment was followed by rinsing and air-drying. The treatment was repeated after a 24 h rest period.

2.3. Thermal treatment

Prior to the thermal treatment the hair was washed with 10% sodium laurylether sulphate (SLES) solution, rinsed and dried by pressing between paper towels. On these initially 'towel-dry' tresses the thermal treatment was applied, using a commercial straightening iron set to a digital reading of 200 °C. The authors are well aware that this is a nominal temperature. However in view of the objectives of the study, no steps were taken at this stage to determine the actual temperature on the surface or inside the tress, which is, however, expected to be reasonably homogeneous [21]. To control the conditions of the treatment, a tress was clamped into a tensile testing machine (Instron, UK) and drawn through the iron such that a total contact time along the tress of 1.67 s was achieved for each pass. For two tresses each, from the groups of untreated as well as bleached tresses, total contact times of 60, 300, and 800 s were realized through repetitions. In view of practical modes of applying thermal straightening, after 30 repetitions each tress was washed, brought to a towel-dry state and the thermal treatment procedure was restarted.

2.4. DSC-measurements

All investigations by Differential Scanning Calorimetry (DSC) were carried out in water, for reasons described elsewhere [33,35]. The measurements were conducted on a power-compensated instrument (DSC-7, Perkin-Elmer, USA), using stainless steel, large volume pans, which are pressure resistant up to 25 bar. The temperature range was 50–190 °C with a heating rate of 10 K min^{-1}. From the hair tresses small subsamples were taken (approx. 100 hairs) and cut into snippets, about 2 mm in length. The snippet samples were stored under standard room conditions and would thus contain about 12% of water [3,36,37]. Under these conditions hair snippets (4–7 mg) were weighed into the DSC-pans and 50 µl of water added. The pans were sealed and stored overnight prior to the DSC-measurement. Data obtained from the measurement were denaturation temperature T_D (peak location) and denaturation enthalpy ΔH_D (determined from the peak area on the basis of a linear baseline). No corrections were applied with respect to the water content of the material. For each hair type 22 data pairs were acquired across the experimental time range. Data analyses were conducted using SPSS (Version 20, IBM Corp., 2011) and Statistica (Version 13, Dell Software, 2015).

2.5. Codes for samples

According to the various steps of preparation, samples are coded as follows:

N0 = natural hair, no thermal treatment (0 s)
N1 = N0 + 100 s cumulative thermal treatment
N2 = N0 + 300 s
N3 = N0 + 800 s
For oxidized, bleached hair sample coding is analogous (B0–B3).

3. Results and discussion

3.1. General observations

After the heat treatment the tresses in the two groups were investigated with respect to their denaturation performance by DSC in water. Fig. 1 gives a typical DSC curve for the natural material (commercial, untreated Caucasian human hair). Upon oxidation, the peak becomes smaller and moves to lower temperatures [34].

DSC-curves for hair in water generally show a single peak with the general occurrence of asymmetry or even a more or less prominent shoulder to higher temperatures. The peak location as such, that is the denaturation temperature T_D, is generally associated with the properties and, namely, the viscosity of the matrix, which kinetically controls