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The effects of esterification on the humidity-dependent glass transition of human hair

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ABSTRACT

Human hair is a highly complex biomaterial. For the analysis of its mechanical and thermal properties it is, however, well described by a two-phase structure, which contains as morphological components the highly-ordered, crystalline intermediate filaments (IFs) and the less-ordered, amorphous matrix. A previous study has shown that wool compared to human hair exhibits for the whole range of water contents higher values for the glass transition temperature, T_g, as a property of the matrix. This is despite a higher content of hydrophobic, high glycine-tyrosine (HGT) proteins contained within the matrix of human hair. On this basis, the internal plasticization (IP) hypothesis was developed, stating that the composition of the matrix is the controlling factor of the glass transition and that, namely, the HGT-proteins may have a plasticization effect in the matrix. To further evaluate this hypothesis, esterifications of the hair proteins with various alcohols were carried out to introduce additional and variable hydrophobic sites into the fiber. The effects of these modifications on the humidity-dependent T_g of hair are analysed on the basis of the Fox-equation. It is shown that all esterifications lead to a systematic decrease of, the T_g-values in line with the IP-hypothesis.

1. Introduction

The structure of the hair fiber is highly complex and exhibits a hierarchical structural system from the α-helical keratin protein chains to the bulk cortex surrounded by the protective cuticle layer. However, in general terms, the hair shaft is made up of three morphological regions: the cuticle, at the surface of the fiber; the cortex, as the major part making up the core of the fiber; and the medulla, a central vacuole-type region which is usually only found in coarser hair fibers. All cells and materials are connected by inter-cellular cement, referred to as the cell membrane complex (CMC) [1].

Within the cortical cells, axially oriented semi-crystalline rod-like structures exist, known as the intermediate filaments (IFs), and these are embedded in an amorphous matrix of intermediate filament associated proteins (IFAPs). To describe the thermal [2,3] and some of the mechanical [4] properties of the hair fiber, it is well established that, the structure of the hair fiber may be simplified to a two-phase model [5], containing axially oriented, filamentous IFs embedded in an amorphous matrix. The glass transition, a property of the amorphous matrix, has been shown to be lowered by water as a plasticizer in keratin fibers [2,6–8]. This is a common phenomenon for proteins [9,10].

The relationship between the glass transition temperature T_g and water content in keratins is well described by the Fox-equation [2,6,11]. The Fox-equation states that the T_g of a polymer/plasticiser blend, in this case keratin and water, is additive in a reciprocal way and a reflection of the glass transition temperatures of the individual components as:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

where T_g (K) is the glass transition temperature and w the weight fraction. Subscripts 1 and 2 refer to keratin (hair) and water, respectively. The equation reflects the straightforward relationship between the T_g of the system and that of its constituents and does not take into account specific interactions. The variability of the T_g-data for keratins [2,6] generally constrains the use of more complex approaches [2].

In a previous study [2] it was shown that the relative-humidity or rather water content (w_2) dependent T_g of human hair is systematically lower than that of wool, yielding glass transition

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temperatures for wool and human hair in the dry state of 174 °C and 144 °C, respectively [2,6]. This is despite a higher content of hydrophobic proteins in the matrix of human hair, which are rich in glycine and tyrosine (HGT-proteins) [12,13]. This increased hydrophobicity would have been expected to lead to a lower sensitivity of the T_g of hair toward water. However, the opposite effect is observed and is attributed to a lower efficiency of hydrogen bonding stabilisation in the matrix in the glassy state. This observation gave rise to the internal plasticization (IP) hypothesis [2], which basically states that hydrophobic proteins act as plasticisers within the matrix of keratins.

This study was intended to investigate this hypothesis by increasing the hydrophobicity of the matrix proteins through esterification of the side-chain carboxylic groups in the hair proteins, namely, of aspartic and glutamic acid. Subsequent to this polymer-analogous modification the effects on the humidity-dependent glass transition of human hair were measured.

Esterification included the modification of the carboxyl side groups using alcohols of varying alkyl chain length (methanol, ethanol, *n*- and *i*-propanol) in order to further investigate changes of the plasticizing effect resulting from different lengths and shapes of the alkyl side chain. As alternative approach, reduction of cysteine and alkylation have also been conducted [14], first results of which have been reported elsewhere [15]. Apart from its academic relevance, internal plasticization through hydrophobic modification has become of increasing interest in the cosmetic industry, as applied research strives to discover more effective methods for hairstyling and hair style maintenance.

The humidity dependent glass transition temperature of hair T_g was determined by differential scanning calorimetry (DSC), according to a well-established protocol [2]. The technique gives experimentally the most straightforward access to T_g and, namely, with recent developments [14] enables the ready application of repeated heating/cooling cycles to the samples. This greatly aids in the identification of the glass transition in human hair, which tends to be difficult to detect. This is due to the fact that the change of heat capacity associated with T_g is rather low ($\Delta C_p \sim 0.1\,J\,g^{-1}\,K^{-1}$) [2] compared to other proteins ($\Delta C_p \sim 0.4\,J\,g^{-1}\,K^{-1}$) [16].

2. Experimental

2.1. Material

All experiments were carried out on commercial brown, European human hair (Kerling Ltd., Backnang, Germany). The hair was in the form of tresses (25 cm long). No prior treatment was carried out on the hair fibers. The fibers were divided into approximately 10 cm long sections for chemical modification.

2.2. Esterification

Esterification was carried out based upon the method for wool by Alexander et al. [17] as reviewed by Maclaren and Miligan [18]. Dry untreated human hair fibers were refluxed under nitrogen in a 0.2 M alcoholic hydrochloric acid solution for 6 h. Anhydrous reagent-grade solvents were used in all cases. The hair to liquor w/v ratio was 1:50. Four separate reactions were performed using methanol, ethanol, *n*- and *i*-propanol, respectively. After modification, the hair fibers were washed under running tap water for 2 h, and then washed (10 × 50 mL) with deionised water.

2.3. Sample preparation

As with all amorphous polymers, the thermal and physical history of the hair fibers affects the glass transition [2,19] as well as the related viscoelastic properties [8]. In light of this, the experimental procedure for the determination of T_g was designed to control physical aging [2].

Hair fiber snippets (1–2 mm in length) were prepared from untreated and esterified hair, ensuring a representative sample along the full length of the fiber. Snippets (5–10 mg) were added to T-zero aluminum DSC pans (TA Instruments, UK) and dried over phosphorus pentoxide for 48 h. The pans were then transferred to desiccators, containing suitable saturated salt solutions to provide a range of constant relative humidities [20], for 1 week at 20 °C. All samples were prepared in triplicate. For the DSC analysis, silicone oil (10–15 μL) was added to the pan, covering the hair snippets to suppress absorption/desorption of moisture during the measurement. The pans were then hermetically sealed.

2.4. DSC

The DSC (DSC Q100, TA Instruments, UK) was calibrated using indium. As a reference for all further measurements, an empty aluminum T-zero pan was used. Samples were heated at a rate of 10 °C/min from 0 °C to a variable final temperature depending on the water content of the sample, ensuring the temperature was safely below denaturation events. The helical proteins in the IFs of human hair denature, depending on the water content of the fiber, between ≈210 °C (dry) and ≈150 °C (wet) [3,21]. Samples were then cooled at the same rate to 0 °C. Two further heating/cooling cycles were performed to improve the success rate of T_g detection. Prior investigations had conclusively shown that T_g and thus by implication water content remained constant during the repeated heating and cooling steps [14].

In order to obtain the glass transition of dry hair, hair fiber snippets (5–10 mg) were added to T-zero aluminum DSC pans and sealed with a perforated lid to allow water to evaporate during the measurement. Initially, the samples were heated at a rate of 10 °C/min to 200 °C, after which two further heating/cooling cycles were performed up to 150–200 °C. The lower temperature of these cycles was adjusted for the various esterified hair types according to the expected T_g-values (dry).

2.5. Water content

In parallel to the DSC sample pans, hair fiber snippets (approximately 200 mg) were added to glass vials. These samples were dried and equilibrated at the various relative humidities as detailed above alongside the DSC samples. Weight readings were taken at various stages of the process until constant mass was achieved. The samples were then dried at 100 °C to constant mass (±1 mg) for 2–3 days. Water weight fraction or water content w_2 was determined by weight difference and is defined as the ratio between the mass of water and the total mass of hair equilibrated at a given relative humidity.

3. Results and discussion

3.1. General observations

Fig. 1 shows a typical DSC-curve of a successful measurement for untreated human hair with a water content of 16%. The glass transition temperature is here defined [22] as the midpoint between the on-set (T_1) and off-set (T_2) temperatures of the transition, as shown.

As part of the investigation ΔC_p-values at T_g were also determined and found to be in agreement with previous analyses [2] and independent of the esterification treatment of the hair.

In line with expectations from investigations for wool [23,24] the relationship between relative humidity (RH) and water content for untreated and esterified hair followed the sigmoidal shape,