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Original article

Variation in the sorption properties of historic parchment evaluated by dynamic water vapour sorption



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ABSTRACT

Understanding the hydration of the collagen historic parchments is of great importance to the conservation and restoration processes. In this study, modern and historic (dated 1817 and 1769) parchments were investigated using dynamic water vapour adsorption/desorption (sorption) experiments. The relationship between the equilibrium moisture content against the relative humidity at constant temperature for two consecutive sorption cycles, the hysteresis and kinetic properties were analysed for different parchments from a historic archive. It was found that historical parchment samples exhibited higher equilibrium moisture content levels throughout most of the hygroscopic range and the hysteresis was greater than that of the contemporary sample. The samples were all found to obey parallel exponential kinetics for both adsorption and desorption. By applying the parallel exponential kinetic model, it was observed that the difference in the hysteresis is apparently mostly due to changes in the collagen matrix relaxation processes.

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1. Research aim

The aim of the research was to examine any differences in water vapour sorption properties between different aged parchment samples and to determine if the sorption kinetics could be evaluated using the parallel exponential kinetic model, which has been successfully applied to the study of cellulosic and lignocellulosic materials.

2. Introduction

Large historical parchment-based collections (sheets, scrolls, manuscripts, codices, books, etc.) are kept in museums, archives or libraries; and in order to ensure the continued preservation of this valuable historical material, it is important to understand the changes which take place in the structure of the material over time [1–4]. Parchment is a complex natural material made from processed, untanned animal (goat, sheep or calf) skin. Traditionally, production of parchment involved removing of the hair in lime

or by soaking in liquors containing vegetable infusions with high pH; washing in water, then thinning and drying under tension [5–8]. The final product contains predominantly collagen, a triple helix structure formed by three polypeptide chains with a known amino acid sequence, stabilised by inter-chain hydrogen bonds, van der Waals interactions and structural water molecules [9], but also some lipids and inorganic matter. The unique structure of collagen imparts excellent mechanical properties and chemical stability to parchment. However, it deteriorates with time, being sensitive to different environmental stresses, such as temperature, humidity, light, microorganisms or/and atmospheric pollutants. These may cause both chemical and photochemical modifications in the material, resulting in parchment deterioration by unfolding of the collagen structure, destruction of its hierarchical internal and surface structure and evolution into disordered gelatine [4]. This leads to fragility and brittleness of aged parchment objects. The formation of gelatine is located on the surface of the parchment or associated with specific features, such as hair holes, the presence of metal-based inks, etc [10]. Since the relationship of collagen and gelatine with water vapour differ, the degradation of parchment results in a change in the sorption properties of the material with time [10]. Gelatine exhibits a random coil geometry and would be expected to have a much greater affinity for water than does collagen because more polar groups are accessible to

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water molecules [10]. However, a study comparing the sorption isotherms of collagen and gelatine showed that gelatine exhibited a lower sorption capacity [11]. Unfortunately, this paper lacks details of how the samples were treated prior to the experiment, which can have a strong effect upon the results obtained [12]. Over time, parchment documents may undergo modifications in structure due to microorganisms and abiotic environmental factors (especially humidity, temperature, oxygen and UV exposure). The effect of oxidation (which may be caused by free radicals from the atmosphere) is evidenced by cleavage of the collagen molecules, which reduces the stability of its structure. Hydrolysis of collagen is another deterioration mechanism caused by the combined action of air pollutants and humidity. Gelatinization may occur when there is a combination effect of water and temperature. An increase in temperature may cause molecular rearrangements, which may further induce breaking of the hydrogen bonds between the collagen chains. Another degradation phenomenon is crosslinking, leading to embrittlement, which may occur during dry heating [13].

Water plays an important role in the chemical modification of parchment during ageing. This affects the structure of collagen by its chemical modification through hydrolysis, solvation of free radicals, hydrogen bond stability, and the rate of gelatine formation [14]; therefore moisture content and the interaction of parchment with moisture is an important aspect for the preservation and storage of the parchment documents. According to the review of Gonzalez and Wess [10], recommendations for the storage RH for parchment vary considerably and there is a lack of a solid scientific foundation underpinning these recommendations.

Characterising historic parchment is a challenging task due to its complex structure, diversity and varying extent of degradation. Even though there are extensive studies of the water sorption properties of collagen powder, skin or leather [e.g. 15–18], studies of the water sorption properties of parchment or vellum are quite limited in the literature. Hansen et al. [14] studied the effect of different relative humidity (RH) levels on the mechanical properties of modern vellum, while Abdel-Maksoud and Marcinkowska [19] investigated the sorption properties of new and historic parchment at 95% RH and 20 °C. They observed different behaviour between new, artificially aged and historic parchment, with the historical and artificially aged parchment showing reduced levels of sorbed water. The rate of change in moisture content (MC) of new and historic parchment was examined by Dernovšková et al. [12]. In this study, they measured the response of historic and new parchment to a step change in RH from 20% to 98% and returning to 20%. The historic parchment exhibited higher levels of MC and faster response times to changes in RH. The water sorption isotherms of parchment were analysed by Facchini et al. [1] along with other techniques in order to investigate the effect of the restoration process of naturally aged and fire-damaged parchments of old manuscripts. The authors used dynamic vapour sorption (DVS) for their studies, but from our experience, the conditions set for the samples to reach the equilibrium (a rate of mass change lower than 0.01% over a period of 30 s) was too short for studies of this nature. This is the reason that the isotherms reported do not have closed loops. In addition, the variation in sample mass (between 20 to 40 mg) was too large to allow for comparability of different samples when using the same equilibrium conditions.

The DVS instrument allows for the possibility of determining the kinetics of the sorption process and it was reported that the adsorption and desorption behaviour of the flax fibre water vapour system using DVS could be accurately modelled using parallel exponential kinetics (PEK) [20]. Subsequently, the PEK model was also shown to provide excellent fits to the data for describing the sorption properties of regenerated cellulose fibres [21–23] and microcrystalline cellulose [24]. The application of the PEK model has also been demonstrated for wood samples [25] as well as a wide range

of plant fibres [26]. The drying kinetics of various foodstuffs also obeys the PEK model [26]. However, the applicability of this model to parchment/collagen has not been studied previously.

The PEK model has a double exponential form, with two kinetic processes taking place simultaneously, the so-called fast and slow kinetic processes. These are described by the equation (1):

$$MC = MC_0 + MC_1 (1 - e^{-t/t_1}) + MC_2 (1 - e^{-t/t_2}) \quad (1)$$

where: MC – moisture content at time t of the sample exposed to a constant relative humidity (RH%), MC_0 – moisture content of the sample at the time 0.

The two exponential terms $(1 - e^{-t/t_1})$ and $(1 - e^{-t/t_2})$, with their characteristic times t_1 and t_2 and the moisture contents MC_1 and MC_2 , are associated with the fast and slow processes, respectively. A summation of MC_0 , MC_1 and MC_2 at any specific RH gives the EMC.

When first introduced, it was thought that the two processes were linked to different types of sorption site in the cell wall [20], but more recently, it was concluded that the processes are actually due to two distinct physical phenomena that, coincidentally, are described by the same mathematical function [27]. Therefore, the fast process is described by a linear driving force mass transfer diffusion model [28], while the slow process is linked to relaxation-limited kinetics, in which molecular relaxation processes in the cell wall macromolecules are the rate limiting steps. Further support for this interpretation of the PEK model being associated with two different physical processes comes from the observation that the PEK model cannot be applied in materials above T_g [29].

The phenomenon of hysteresis in natural materials can be explained by a model first introduced by Vrentas and Vrentas [30] to describe sorption hysteresis in glassy polymers below the glass transition temperature (T_g). It has been postulated that there is a link between the sorption kinetics and sorption hysteresis phenomena [31]. In the model described by Vrentas and Vrentas [30], the origin of hysteresis is explained by the way that the matrix of the sorbate reacts to the ingress and egress of sorbent molecules. During adsorption, the incoming molecules penetrate into the matrix creating micropores (pores with width not exceeding about 2.0 nm [32]) within the structure, requiring molecular rearrangements to accommodate the sorbent in that structure. When the molecules exit during desorption, the micropores within the structure collapse, again requiring molecular rearrangements within the matrix of the sorbate. It is known that micropores between 1 and 10 nm exist within the structure [33] and it is onto the internal surface of these micropores that the water is adsorbed. Relaxation of molecular segments within the structure to accommodate the sorbed water molecules relies upon there being sufficient void volume surrounding these relaxing elements. Below the glass transition temperature, there is insufficient void volume around the relaxing segments of the matrix molecular network to allow for instantaneous rearrangements. This time lag ensures that the sorbate is in two different energetic states between adsorption and desorption. The origin of hysteresis can then be attributed to a kinetic phenomenon occurring on molecular time scales. This model predicts that as the difference between the isotherm temperature and the T_g decreases, there is a corresponding reduction in sorption hysteresis, as has been observed [25]. The model also predicts that sorption hysteresis should collapse when the T_g of the material is reached, as has also been recently demonstrated [29]. The T_g of gel materials, such as collagen, will decrease with increasing moisture content, because the swelling of the micropores caused by the presence of the sorbate in the matrix creates void volume around the relaxing segments. This suggests that there should be a link between the phenomenon of sorption hysteresis and the slow sorption kinetic process, which has been attributed to molecular relaxation. The theoretical support for this hypothesis

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