



## Diffusion of permanent liquid dye molecules in human hair investigated by positron lifetime spectroscopy

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### ABSTRACT

The diffusion behavior of a commercial permanent liquid hair dye in human hair has been investigated using positron annihilation lifetime spectroscopy (PALS) and gravimetric sorption method. The positron technique makes it possible to non-invasively characterize the angstrom sized free volume holes in hair, which are supposed to be express pathways for diffusion of small molecules. The o-Ps lifetime parameters  $\tau_3$  and  $I_3$  decrease rapidly during the first 60 min of sorption time. The overall decrease in o-Ps lifetime ( $\tau_3$ ) was well over 200 ps and o-Ps intensity ( $I_3$ ) drops by 3.5%. These positron results are explained in terms of dye molecules filling the free volume holes and hair morphology. The dye penetrates the cuticle rapidly, but slowly in cortex. The first hour of dyeing appears to be the most effective period of deposition of dye molecules within hair. These results are well corroborated by the sorption results which suggest that the dye diffusion is essentially a diffusion controlled (i.e. Fickian) process, with no observable relaxation effects. In the latter part of the sorption, where positron parameters remain almost constant, mass increase might be due to surface adhesion. These two stages of sorption are well separated by the positron technique. The sorption curve also yielded an average value of apparent diffusivity of the dye in hair. From this study, we conclude that the free volume theory and positron technique, widely used in polymer research, may expediently be used to understand hair properties, more importantly diffusion of dye molecules.

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### 1. Introduction

Permanent hair coloring is a popular cosmetic practice of achieving a shampoo resistive, non-fading surface coating of hair shaft. Its success lies in the formation of larger dye molecules *inside* the fiber which remain embedded even after repeated washings. Small organic molecules of the dye formulation penetrate the fiber and react chemically to form dye molecules. The condensation reactions that occur are relatively fast compared with diffusion [1] and hence the overall sorption of these molecules is controlled by diffusion rather than by the reaction.

Information regarding the rate and extent of penetration of the ready-made liquid dye and the consequential hair damage are essential inputs for cosmetic industry to aid improvements. However, not many physical methods are available to follow this complex diffusion process for human hair.

Literature reports [2] suggest that well-defined penetration pathways exist within hair and molecules progress along these preferred routes and gain access to fiber interior. As molecules need

room for motion, these pathways may probably be an interconnected network of voids or micropores that arise due to structural organization of hair components. Then it becomes interesting to know about the void content and their distribution within hair and importantly the influence they have on the bulk properties of hair (e.g. diffusion). However, information on these microvoids is rather difficult to get due to their small size and lack of suitable and sensitive microprobes. In particular, no reports are available on accurate measurements of the angstrom sized 'free volume holes or voids' in human hair.

Hair being a biopolymer, it is natural that the molecular architecture results into microvoids called free volume holes or cavities. These are low electron-density regions existing mainly in the amorphous domains of a polymeric material [3,4]. They may be present as pre-existing holes or dynamically formed under external influence, by rearrangements of polymer chain segments. A free volume is defined as the difference between the total volume and the occupied volume of the polymer [5]. The amount of free volume in a polymer is called the fractional free volume ( $F_v$ ) or free-volume content. According to Fujita's free volume theory [6,7], which owes its origin to Cohen and Turnbull [8], the rate of diffusion of a molecule depends primarily on the ease with which the polymer chains exchange their positions with the penetrant molecules. The mobility of the polymer, in turn, depends on the amount of free

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volume in the matrix and thus relates the diffusion coefficient to the fractional free volume of the system. This simple theory has been tested and found to describe the diffusion of a number of organic, inorganic molecules and vapors in polymers satisfactorily [7,9,10]. More recent theory on these lines is the one due to Mauritz et al. [11]. This is also a free volume based, molecular shape-dependent diffusion theory for large molecules in rubbery polymers. In the rubbery state, polymers can be viewed as being in a dynamic fluid-like state and the penetrant molecule can be envisioned as “swimming” through its liquid-like medium [12]. Further more, this theory dwells upon the concept of combining free volume and energy-activated diffusion which was addressed earlier by the Meares' model [13].

The free volume model is a well-established one in polymer research as it is widely used to understand a variety of polymer properties [4,9,10,14–18], notably diffusion. Of all the physical techniques used to characterize free volume holes, the positron annihilation lifetime (PAL) technique is most favored due to its high sensitivity and unique capability of measuring both the average size and number density of free volumes. The method is non-destructive, and requires no special sample preparation.

In brief the positron lifetime method can be explained as follows: When an energetic positron enters a condensed medium like a polymer or a biopolymer (hair), it thermalizes quickly and thereafter annihilates with the electrons of the medium via free annihilation or from a localized state (trapped state) or forms a bound state with an electron called positronium (Ps) atom. The free annihilation is the one in which positron annihilates with an electron of the medium, without getting trapped into defects of the medium. Free annihilation lifetime is of the order of 200 ps. Secondly, some of the positrons may get trapped into defects like voids and annihilate in a time ranging from 200 to 500 ps. The bound state of Ps can exist in two spin states. The para state (p-Ps) (particle spins anti-parallel) annihilates with a lifetime of 125 ps. The ortho state (o-Ps) (particle spins parallel) annihilates with a lifetime of 140 ns. In condensed matter, o-Ps annihilates mainly into two photons by a pick-off mechanism in which the positron of o-Ps annihilates with an electron of opposite spin from the surrounding molecules; thereby, its lifetime is reduced to a few nanoseconds. The lifetime of o-Ps depends on the overlap of the Ps wave function with the electron wave function of the free-volume cavity. Hence, the larger is the hole size, the smaller is the overlap and, hence, the longer the lifetime. So, the o-Ps pick-off lifetime ( $\tau_3$ ) and its intensity ( $I_3$ ) are a measure of the free-volume size and their number density, respectively [4].

Hair is a heterogeneously composed natural semi-crystalline polymer of  $\alpha$ -keratin. The major portion of its bulk (the cortex) consists of crystalline microfibrils embedded in a larger amorphous matrix [1]. Surrounding cortex is cuticle, a protective covering ( $\sim 5 \mu\text{m}$  thick) of 8–10 layers of overlapping cells. The matrix and the non-keratinous regions (mainly cell membrane complex (CMC) and endocuticle) of hair undergo large volume swelling in aqueous solution [1,2] and hence may be regarded as preferential sites of free volume cavities. However, the free volume theory has not received much attention in hair research, as it is believed to be too naïve for use on a complex system like hair [19]. But we believe that the limited success of the model is due to in-sensitive methods employed to quantify voids in hair and hence are interested to testify, through this study, the utility of the free volume model in understanding hair properties, specifically diffusion of dye molecules of cosmetic interest.

The objective of the present investigation is to understand the kinetics of the diffusion process making use of the conventional gravimetric sorption method, combined with a novel and well established tool namely the positron annihilation lifetime spectroscopy (PALS) used to study human hair for the first time.

## 2. Experimental

### 2.1. Materials

Virgin black hair was obtained from the head of a healthy Asian lady who had no special cosmetic hair treatments such as permanent waving, bleaching or dyeing. The dye used was a popular, branded permanent liquid hair dye purchased from a local shop. The dye was supplied as a two-component kit: one containing precursor/coupler mixture and the other a developer solution (stabilized hydrogen peroxide). The dye was prepared, just before usage, by mixing equal proportions of the two components, as instructed by the manufacturer.

### 2.2. Preparation of hair sample

The long hair tress, trimmed at the distal end, was suitably divided and cut, and made into small bunches weighting 1.4 g each and having a length of about 6 cm. The hair fibers were held tightly at one end by carefully applying a thin film of good quality adhesive. The bundles were washed in a shampoo solution and thoroughly rinsed with distilled water and then dried for a minimum of 48 h at room ambience where the relative humidity was about  $60 \pm 2\%$ . A pair of such bundles forms *one sample* for use in sorption and positron lifetime measurements. All weight measurements were made using a digital balance (Sartorius, MC1, LC620 S), with a precision of  $\pm 1$  mg. One of these samples was used as control and the remaining were used for dyeing.

### 2.3. Dyeing treatment

Samples were immersed in excess volume of the freshly prepared dye solution contained in an airtight plastic bowl for different known intervals of time. The solution was kept agitated throughout. The samples were then removed from the dye bath, and immediately washed under running distilled water for 10 min. The washing procedure was kept uniform, as far as possible, for all the treated samples. The samples were dried at room ambience.

### 2.4. Measurements

#### 2.4.1. Average fiber diameter

Diameters of hundred fibers of the control sample selected randomly were measured with a micrometer screw gauge. The average value was found to be  $76 \mu\text{m}$ .

#### 2.4.2. Dye sorption

The weight of the untreated (virgin) and the corresponding dye treated samples were determined using digital balance accurately up to a milligram. The amount of dye uptake ' $M_t$ ' in dyeing time ' $t$ ' was calculated by subtracting the two weights. The sorption experiment was continued until mass uptake by the fibers reached an equilibrium value ( $M_\infty$ ).

#### 2.4.3. Positron lifetime measurements

Positron lifetime measurements were carried out using a standard fast-fast coincidence system with conically shaped  $\text{BaF}_2$  scintillators, coupled to photomultiplier tubes of type XP2020/Q with quartz window as detectors. The coincidence lifetime spectrometer had a time resolution of 220 ps. All measurements were made at room ambience. The source-sample sandwich geometry was used for positron lifetime measurements, wherein one hair bundle of a given sample was placed on either side of the source and the resulting sandwich was held together tightly by a pair of clampable rectangular aluminum plates that had circular holes at the centre in line with the source spot (about 2 mm in diameter

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