Review Article

Hair colouring, permanent styling and hair structure

S Harrison & R Sinclair

Department of Medicine (Dermatology), St. Vincent's Hospital Melbourne, Fitzroy, Victoria, Australia

Summary

Hair is an important component of body image and has immense psychological importance for both men and women. Women, in particular, over the ages have modified their appearance through changing their hair colour or style. Hair can be straight, wavy or curly, blonde, black, brown or red. These natural variations are an important part of our identity that can be manipulated according to the dictates of fashion, culture or society.

Different types of hair have varying affinity for the different colouring and waving methods. Damaged hair also has a different affinity for hair products than normal healthy hair. The hair shaft is remarkably strong and resistant to the extremes of nature. Hair cosmetics are widely available and manipulate the structural properties of hair. Whilst most procedures are safe, there is considerable potential for damage to the hair and hair problems of acute onset, including hair breakage, hair loss and loss of condition, are frequently blamed on the last product used on the hair. Hair problems are particularly prevalent among people who repeatedly alter the natural style of their hair.

Keywords: bleaching, hair colouring, hair cosmetics, hair structure, permanent waving, straightening

Introduction

Although hair has no vital function, it plays a very important role in self-image. Hair is one of few physical characteristics we can change and manipulate to the dictates of culture and fashion. Hair cosmetics are widely used and manipulate the structural properties of the hair. The structure and protein constituents of hair give rise to the physical properties of hair. Hairs have a structural organization with an outer layer of flattened cuticle cells surrounding the elongated polyhedral cortical cells. The cortical cells surround a central optional core of medullary cells. It is the cortical layer that determines many of the mechanical properties of the hair. Successful cosmetic alteration of the hair requires that the chemical processes alter the normal structure of the hair shaft. For a permanent change in the hair, the chemical reaction of colouring, perming or straightening must occur in the cortex. Bleaching, perming and straightening alter the physical properties of hair. The disulphide bonds of the hair shaft are chemically broken in hair styling with permanent waves and straightening and then reformed once the desired change is brought about so that the new style is maintained. A large variety of cosmetic preparations is available and are used regularly by most of the world's population without any adverse effects. However, any chemical treatment, normal grooming habits and environmental exposure can produce changes in hair texture or hair breakage. These changes can be seen microscopically as weathering of the hair shaft and contribute to rendering the hair structurally weaker, more prone to tangling and rougher in appearance.

Correspondence: Dr. Rodney Sinclair, St. Vincent's Hospital Melbourne, Department of Dermatology, PO Box 2900, Fitzroy, Victoria 3065, Australia, E-mail: rod.sinclair@srhm.org.au

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Hair shaft structure

The hair is an epidermally derived structure comprising the hair follicle and the hair shaft. The hair follicle is not affected in cosmetic hair procedures. Cross-sectionally

the hair shaft has three major parts from outside to inside – the cuticle, the cortex and the medulla. The main constituents of hair are protein, lipid, water, melanin and trace elements.[1]

The cortex is the main bulk of a fully keratinized hair shaft and contributes most to the colour and the mechanical properties of the hair.[1] The cortex consists of closely packed spindle-shaped cortical cells filled with keratin filaments, that are orientated parallel to the longitudinal axis of the hair shaft,[1] and an amorphous matrix of high-sulphur proteins.[2]

The intermediate filament hair keratins (40–60 kDa), comprising 400–500 amino acids residues in heptad sequence repeats, form hard keratin polypeptide chains which pair together to form protofilaments.[3] Multiple protofilaments make up a keratin chain. The keratin chains have a large number of sulphur-containing cysteine residues. Cysteine residues in adjacent keratin filaments form covalent disulphide bonds forming a strong crosslink between adjacent keratin chains.[4] The disulphide bonds contribute much to the shape, stability and texture of the hair. These disulphide bonds remain intact when the hair is wet allowing the hair to resume its original shape. Other weaker bonds link the keratin polypeptide chains together such as Van der Waal interactions, hydrogen bonds and coulombic interactions known as salt links.[4] These weaker bonds can be overcome with water.[4]

The cuticle consists of six to eight layers of flattened overlapping cells with their free edges directed upward to the tip of the hair shaft.[1,2] The normal cuticle has a smooth appearance, allowing light reflection and limiting friction between the hair shafts (Fig. 1). It is responsible for the lustre and texture of the hair.[5] The cuticle may be damaged by frictional forces like brushing, combing or blow-drying.[1] Cuticular disruption with alkaline chemicals is the first step in permanent hair styling.[5] If the cuticle is damaged there is little change in the tensile properties of hair,[6] however, damage to the cuticle may compromise its protective function.

In human hair, typically only terminal hairs demonstrate the presence of a central medulla. The medulla may be continuous, occur intermittently along the hair shaft or be absent.[2] It consists of specialized cells with air spaces. The primitive insulating function of the medulla is now redundant and this layer plays no role in the process of hair cosmetics.[1]

Hair colour is determined by the melanocytes found only in the matrix area of the follicle at the base of the cortex directly above the follicular papilla. The melanin pigment is found in the cortex of the hair and is only transferred to the cortical cells during anagen.[3] Eumelanin is the main pigment found in black/brown hair and pheomelanin is the predominant pigment found in blond/red hair.[3] Greying of hair is a normal manifestation of ageing. It is due to the progressive reduction in melanocyte function rather than number.[7] The proportions of eumelanin and pheomelanin and the total amount of melanin determine the final natural colour of the hair.[7]

The hair shaft documents the history of the cosmetic practices of an individual.[8] Hair grows at ≈ 1 cm per month, and so the tip of a hair 24 cm in length, is in fact 2 years old.[8] Therefore, newly growing roots have different properties to the hair tips. The older part of the hair shaft, particularly the tip has undergone over 700 washes, the application of hot styling implements and other cosmetic procedures like colouring and perming, and may show features of weathering, whilst the root may be less porous and have different chemical properties.[8] Weathering is the progressive degeneration from the root to the tip of the hair of the cuticle and then later the cortex due to routine everyday wear and tear. Although all hair exhibits some degree of weathering, longer hair shows more severe changes of weathering (Fig. 2).[8]

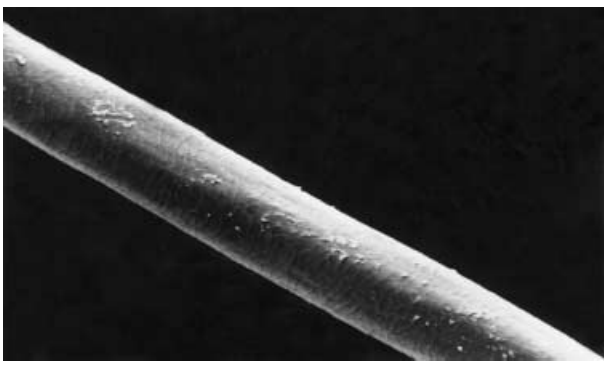

Figure 1 Scanning electron micrograph showing a normal overlapping intact cuticle.

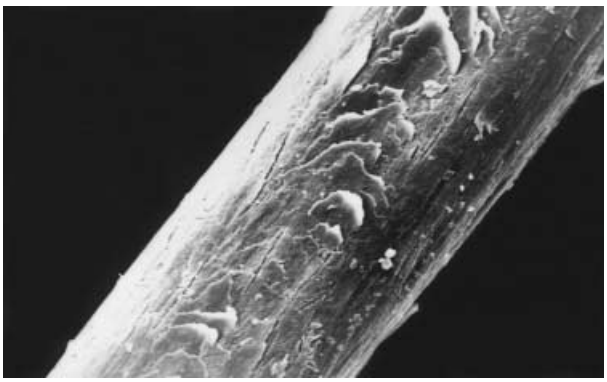

Figure 2 Scanning electron micrograph demonstrating weathering of the cuticle with lifting of the cuticle cells.

Features of weathering include a damaged broken cuticle, longitudinal fissures known as spilt ends and transverse fissures resembling the nodes seen in trichorrhexis nodosa.[2]

Hair colouring

Hair colouring is widely used by women and men either to change their natural hair colour, to delay the onset of grey or to re-pigment already grey hair. A wide variety of natural and synthetic hair-colouring agents is available. Vegetable and metallic dyes are natural colourants, but these have largely been replaced by synthetic organic dyes. The size of the colouring molecule, the swelling of the hair at the time of application and the basicity of the dye determines whether the dye penetrates the cortex or precipitates on the cuticle.[9] The most successful dyes are small, basic molecules. Hair dyes are classified according to their resistance to washing and the length of time the colouring will remain on the hair: permanent, semi-permanent, temporary and gradual. Hair dyes can last longer on chemically treated hair as this hair is porous and unexpected colours can result on chemically treated hair.[5]

Henna is the most common natural dye used to give hair an orange / reddish shade, whilst chamomile yields a yellow dye.[10] Other natural dyes from walnut or logwood are used in Asian counties to blacken graying hair. Metallic dyes using the salts of silver, lead or bismuth were traditionally used by men, as the colour change occurs gradually and use is limited to darkening the hair.[11] However, this type of colouring is unpredictable and a characteristic sulphur smell is produced in the dyeing process.[11] The metals are thought to interact with cysteine in the cuticle to form metal sulphides[10] and the deposits gradually accumulate on the cuticle producing brittle, dull hair.[5] They cannot be removed without damage to the hair and should be left to grow out. Natural dyes are becoming obsolete due to the range of natural-looking colours that synthetic dyes can provide.

A large variety of colours of temporary dyes is available. Temporary dyes can be used for special effects, to add colour highlights, to remove yellow tones from grey hair and to cover small amounts < 15% of grey hair.[5] They last about one week and wash out with one shampoo. They are high molecular mass, water-soluble, acidic molecules that do not penetrate the cuticle and instead deposit on the surface of the hair.[5] These formulas are easy to use and carry little risk of contact dermatitis.[5] However, these dyes readily stain the scalp and skin. Rinses are applied immediately after shampooing, and gels, mousses and sprays are applied on towel-dried hair and are left on.[5]

Semi-permanent dyes are synthetic, intrinsically coloured, low molecular mass coal tar dyes and may also contain para dyes.[5] They are used frequently at home and to brighten a natural colour or modify or cover grey. They are, however, unable to lighten hair as they do not contain any bleach.[5] This dyeing process involves no chemical oxidative reactions. The colouring mixture is blended with a compatible alkaline solution to reach a pH of 9–10 which enables diffusion of the dye molecules into the cortex.[10] Application is simple with the dye applied to the hair like a shampoo and left on the hair for 10–40 min before being rinsed off.[10] The colour usually lasts for 4–6 weeks unless the frequency of shampooing is daily.[5] To ensure homogeneous colouring between newly growing hair and weathered hair, several dyes of the same approximate colour and of different molecular masses are blended to ensure that dye penetrates both the weathered tips and the hair roots.[10] Semi-permanent dyes have the potential to cause allergic contact dermatitis and according to FDA regulations statutory warnings and instructions to perform a skin patch test before use should be present on the packaging.[5]

Permanent dyes are the most common form of hair colourant used. Permanent colouring can obtain nearly any shade, cover any amount of grey and can lighten or darken the natural hair colour.[5] Re-dying is needed every 4–6 weeks to cover regrowth.[5] Permanent dyes have the potential to damage the hair shaft.[5] Alterations in the cuticle ranging from minimal changes (Fig. 3) to severe damage including total loss of the cuticle may be seen with the use of permanent dyes (Fig. 4).[12] The dye mixture is applied to the hair and left on for 20–40 min before being washed off with water. The colour results from an oxidative reaction within the hair shaft.[5] They are available as a liquid, cream or gel.[13] All permanent dyes utilize a series

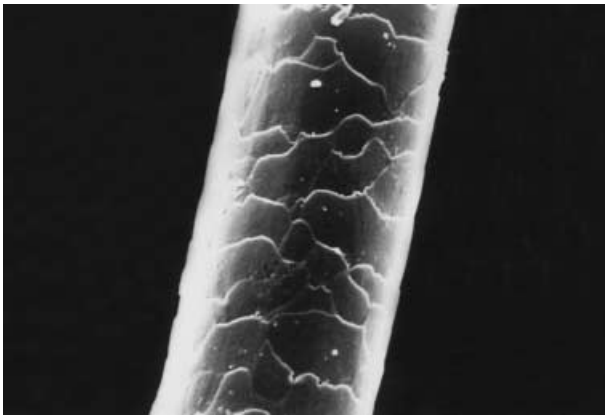

Figure 3 Scanning electron micrograph showing minimal weathering of the cuticle with chipped cuticle cells.

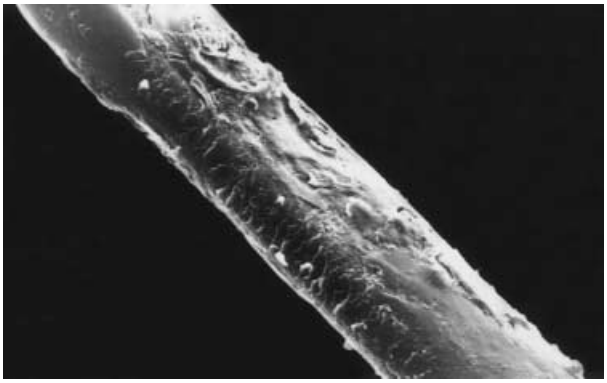

Figure 4 Scanning electron micrograph demonstrating severe weathering and loss of the cuticle.

of chemical processes within a single application and all forms must be mixed with hydrogen peroxide before application, without which they are ineffective.[13] The permanent dyeing process requires three steps: primary intermediates, couplers and oxidants.[10] Typical primary intermediates available are the para dyes such as aminophenols and phenylenediamines (PPD). The primary intermediates form colour on oxidation by hydrogen peroxide.[5] The products of oxidation of the primary intermediates are then reacted with couplers to form indo dyes. Commonly used couplers are phenols, meta-aminophenols and meta-diaminobenzenes.[10] This process depends upon the development of large coloured complexes forming in the cortex and the cuticle. Permanent hair dyes are highly alkaline solutions that cause the cuticle to swell to allow penetration of the dye molecules into the cortex.[14] As the resulting coloured complexes are then too large to diffuse out of the cuticle, the colour is permanent and irreversible until the hair grows out.[10] This process is sufficient to permanently darken the natural colour of the hair. Permanent dyeing to achieve a lighter shade of the natural hair colour requires a two-step process.[5] The hair must first be bleached by a solution containing hydrogen peroxide and ammonium and potassium persulphate. Once the hair is bleached the dye can be added.[14] Lightening dyes tend to contain 30 vol. (9%) hydrogen peroxide.[13] Covering dyes that will darken the hair use a weaker strength hydrogen peroxide of 20 vol. (6%) to be effective.[13] The peroxide not only colours hair, it also can destroy colour. With subsequent colouring, destruction of the pre-existing dye occurs, so that the colour intensity remains stable.[10] The dyes also contain a conditioner to protect the hair from damage, and surfactants, solvents, antioxidants and metal-chelating products for safe, stable storage. The hydrogen peroxide is packaged separately and is mixed with the dye preparation just before use.[10]

Bleaching

Bleaching permanently lightens the natural colour of hair. It can be used in combination with permanent dyeing.[5] Bleaching oxidizes the existing melanin in the cortex. Darker hair requires longer bleaching times. Red hair is more difficult to bleach than brown hair.[10] Hair bleaches consist of hydrogen peroxide of up to 12% strength.[14] They also contain a booster such as ammonium persulphate or potassium persulphate.[5] The hydrogen peroxide is an oxidizing agent that releases oxygen from the hair shaft. The amount of lightening obtained is related to the amount of oxygen released.[5] Bleaching is damaging to the hair causing weakening and a change in texture of the hair. The oxidization reaction destroys some of the disulphide bonds within the keratin and can damage the cuticle making it more porous.[14] A conditioner can alleviate these changes to some degree.[10] The resulting colour is often flat and difficult to control and toners (dilute solutions of dyes) are used to make the colour more aesthetically acceptable.[10] After bleaching, consideration should be given that different parts of the hair may be in different chemical states and the effects of further chemical treatment can be exaggerated, as the cuticle is more porous after treatment with bleach.

Permanent styling

Permanent styling is achieved through the use of permanent waving or straighteners. Both processes involve the denaturation of the structural disulphide bonds of the hair and as such have the potential to cause significant damage to the hair. They also remove covalently bound surface lipids, changing the surface of the hair from hydrophobic to hydrophilic in order to allow the interaction of water and styling products.[8]

Permanent waving has been defined as the chemical process of changing the shape of the hair so that the new shape persists through several shampoos.[15] To permanently alter the shape of one's hair, a certain number of structural disulphide bonds need to be broken.[16,17] The newly growing hair will not be affected by this styling and will maintain the original shape of the hair so the perm will eventually grow out. The perm must be repeated to maintain the wave.

The first step of perming involves wetting the hair and applying rollers with the desired amount of curl. Water extends between the hydrogen bonds of adjacent keratin polypeptides and allows temporary re-shaping to be carried out. The degree of curl predominantly depends on the size of the rollers and the size of the strand of hair wrapped around the roller. Increasing the time of the

perm up to 20 min increases the degree of curl, but further increases in time do not increase the curl.[5] The perm solution is usually alkaline and is applied to the hair once it is set in rollers. There are different types of perming solutions available to cleave the disulphide bonds, the thioglycollates and the bisulphites, but the chemical process involved is the same.[14] These reducing agents work in an equilibrium reaction to cleave only a certain number of the disulphide bonds of the hair shaft. Not all these bonds should be broken and if the reaction goes to completion, the reduced hair does not recover even after re-oxidization.[16] The perm solution is then washed off and a neutralizing oxidative agent like hydrogen peroxide is applied to the hair.[16] New disulphide bonds form in the new shape of the hair.[16] After perming there can be a sulphurous odour, particularly from the thiols, that can persist for a few weeks or longer, so some manufacturers add a perfume to the perm solution, but this is a potential allergic contact dermatitis risk. It has been reported that the neutralization process may be more damaging than the thiol reduction and free radicals may cause some of this damage.[16] Internal hair lipids in cell membranes are also lost during permanent waving.[16]

Straightening can be achieved by chemical or physical methods. The practice is very common in the Black population. Pressing is a process that dates back to the 1800s and was developed by Madame C J Walker who used metal pressing combs or round tongs after application of an oil- or petroleum-based ointment to the hair, to straighten hair section by section. After straightening, the hair was curled with a hot metal curling iron. Hot combing only provides temporary straightening. Advancements in this process have been made in the improvement of the combs, flat irons and curling wands and the introduction of electric implements. The pressing oils have also been improved leaving the hair less greasy.[18] Pressing oils act as heat transferring agents and the heat allows breakage of the disulphide bonds allowing the hair to be moulded straight. Hot comb scarring alopecia can occur following this process as the hot wax damages or destroys the hair follicles.[19]

Chemical hair relaxing or lanthionization is similar to permanent waving, but the hair is permanently straightened instead of curled.[13] The process relies on the cleavage of disulphide bonds to allow the hair to relax and be pulled straight. Once the relaxing agent is applied the chemical process begins. The alkaline relaxer penetrates the cortex and breaks the structural disulphide bonds of the hair. Breakage of the disulphide bonds allows the hair to be mechanically straightened. Reformation of the new disulphide bonds occurs after the relaxing agent is rinsed off and a neutralizing solution (slightly acid) is applied to the hair.[13] These new bonds hold the new shape of the hair. Relaxed hair can now be permed.

Relaxers consist of three components: an alkaline phase, an oil phase and a water phase.[13] The alkaline phase may be sodium or lithium hydroxide, or guanidine hydroxide. The oil phase protects the scalp from irritation. The relaxing agent is a thick cream that facilitates application and in maintaining the hair in a straight position during the procedure.[20] Relaxing agents can be lye-based or non-lye based. Lye relaxers use sodium hydroxide as the alkaline agent. The no-lye relaxers use either lithium hydroxide or a mixture of calcium hydroxide and guanidine carbonate to form guanidine hydroxide.[13] Relaxing agents have the potential to cause irritant contact dermatitis and guanidine hydroxide is usually less irritating. Different hair types require various times of relaxer application. Hair straightening needs to be repeated every 4–6 weeks and only new regrowth needs to be straightened, otherwise damage to the hair can occur.[20] Conditioning may help excessive hair breakage.

Conclusion

Hair cosmetics are widely used by both women and men. Proprietary cosmetic formulations are extensively tested prior to consumer use. Given their widespread use, hair problems are uncommon overall, however, they tend to affect those individuals who style and colour their hair frequently. Permanent styling is more damaging to hair than temporary cosmetic alterations. Individuals may present with an acute on chronic hair problem, but only blame the last cosmetic product or process used, as they have failed to recognize the pre-existing or accumulated hair damage related to the use of other products or processes. It is important to understand the processes of colouring and permanent styling to enable an accurate clinical assessment of the patient's hair.

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