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Semi-permanent split end mending with a polyelectrolyte complex

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Synopsis

Split ends form through mechanical stresses during grooming procedures and are more likely to appear in hair damaged as a result of excessive combing forces. Although there are no conventional systems that will permanently mend split ends, a semi-permanent mending composition has been achieved through a polyelectrolyte complex. The complex is formed as a result of the ionic association of a cationic polymer, Polyquaternium-28, and an anionic polymer, PVM/MA Copolymer. Hair tresses containing tagged split ends are used in measuring mending efficacy. The tagging allows the fate of the split ends to be determined after different types of treatment regimens which test the durability of the mend. Monitoring of the repair and mending durability is carried out with the aid of a stereomicroscope. Results obtained with this method indicate that the complex both by itself and when formulated into a simple lotion provided a high level of split end mending not only after initial treatment but more importantly after combing showing the durability of the mend. Cumulative effects and durability to washing indicate that the polymer complex does not build up on the hair and rinses off with shampoo making possible its usage as a post shampoo treatment. The formulated lotion has higher durability performance as compared to a commercial product with a split end mending claim. The proposed mechanism of action entails a crosslinking microgel structure that infiltrates the damaged hair sites binding them together. This model is supported by the analysis of phase behavior, viscometry, Scanning Electron Microscopy, and absorption of ionic dyes.

INTRODUCTION

The manifestation of damaged hair as seen macroscopically as we view whole hair attributes is based on the state of each of the individual fibers taken collectively. Different types of damage are observed on a microscopic scale using scanning electron microscopy as a diagnostic tool (1). These consist of transverse fractures through the hair's cuticle, transverse fractures of the whole fiber, delamination within the cuticle, longitudinal splitting of the hair shaft (split ends), and multiple longitudinal splitting of the hair shaft (trichorrhexis nodosa) (2). Each of these structural maladies when multiplied by the number of fibers is portrayed in whole hair attributes such as dullness, lack of manageability or stylability, rough texture, and poor combability. The hair as a whole based on the state of the individual fibers looks unhealthy.

There are multiple causes for this damage and encompass physical, chemical, and environmental factors. Versatility of hair styles is a major cause of the predominance of hair damage. Consumers desire products that allow them to express their individuality and personal style to a greater extent. Keeping up with the latest hair style fashion includes oxidative hair coloring and permanent waving. Also styling agents in combination with styling implements such as curling and flat irons allows one to have a different hair style even from one day to the next. The result of this increased amount of styling has its effect on the quality and condition of the hair. This is compounded with longer hair styles since the ends of the hair are older and have experienced more weathering as well as the aggressive styling treatments. Eventually the hair becomes dull, unmanageable, coarse to the touch, and hard to comb. When viewing these damaged fibers on a microscopic scale one realizes the cause of what is observed on the macroscopic scale. With the predominance of aggressive styling behaviors it is clear that there is a market need for compositions and products that are able to not just prevent hair damage but, what is more challenging, affect its repair.

One manifestation of damage that affects whole hair attributes are fibers that have split longitudinally at their tip ends. The technical term for split ends is trichoptilosis. The theory of split end formation as proposed by Swift is fully elaborated in an article entitled Mechanism of split—end formation in human head hair (3) and is depicted in Figure 1. A clue that led to the theory on the mechanism of split end formation was from an SEM of a split end fiber. It was observed that the split occurred in such a manner that it formed parallel to the major axis of the hair diameter (4). Swift theorized that when hair is combed the elliptically shaped hair fibers preferentially orientates so that the major axis is parallel to the surface of the comb tooth. As the comb traverses the hair, shear stresses are produced parallel and longitudinal to the major axis of the fiber. The degree of shear stress is distributed parabolically along the minor axis of the hair so that the shear plane suffering the most shear stress would be that running parallel to the major axis of the hair. When the shear force becomes great enough tiny fractures occur along this axis and eventually will propagate to the end of the fiber. As the comb is pulled through the hair the bending is propagated from root to tip; it is not a static bend. As the comb reaches the tip end of the tress the collection of fibers tend to snarl increasing the shear stresses to a greater extent at the tip than anywhere else along the fiber length. Fibers are dynamically bent over 180 degrees as observed under a stereo-

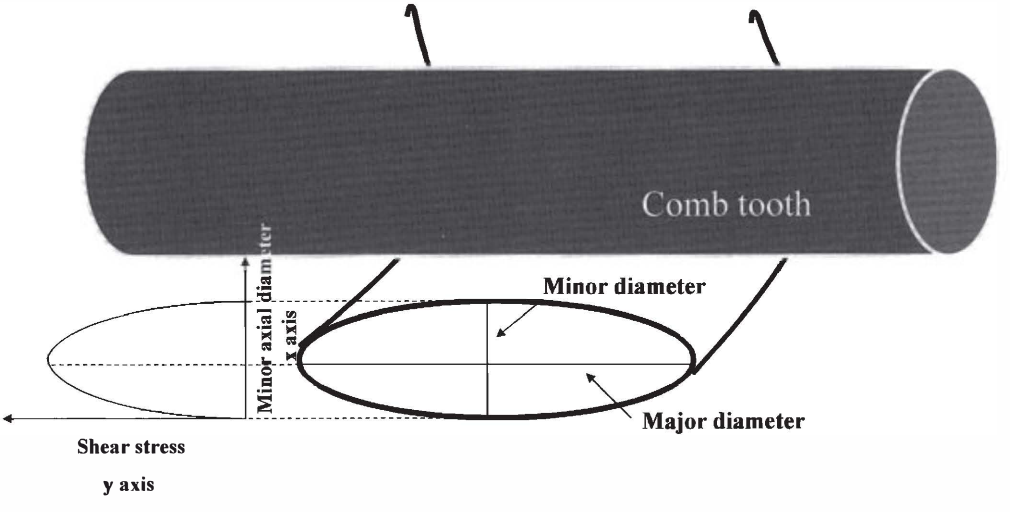


Figure 1. Mechanism of split end formation showing the distribution of shear stresses in fiber during combing. Depiction of theory proposed by Swift (3).

microscope (Figure 2). The major stress then leading to hair fracture is not just one of stretching such as is measured by tensile strength, but rather flexure or bending (5).

Combing, then, is the major route that fibers tend to split since these shear forces are necessary to fracture the hair which eventually will lead to a split end. However there are many factors which weaken the hair that predispose it to split during the combing process (6). There are many references on the effects of UV on the degradation of the different structures of hair. One reference is a review of our current understanding of the subject and options for photoprotection (7). Other damaging factors that are noteworthy to mention are chemical processing such as bleaching (8), thermal (9), thermal-mechanical damage (brush and blow dry) (10), and damage from surfactants which can be translated to multiple shampooing (11). Even if hair has not been purposely damaged, the hair at the tip end being older than at the root has suffered more wear and tear and would tend to split during combing. It is necessary therefore when designing a test method that will be used to test the efficacy of a composition to mend split ends to incorporate into the procedure the same combing forces that are present during everyday grooming. Without this the fibers will not be subjected to the same degree of shear forces during combing and the durability of the mended fiber cannot be assessed.

This aspect of testing the durability of the split end mend has been incorporated into the test method used in this study. Subjecting hair to realistic combing forces allows the assessment of not only the initial mending after treatment, but more importantly the durability of the mend such as a post combing treatment. With this method various

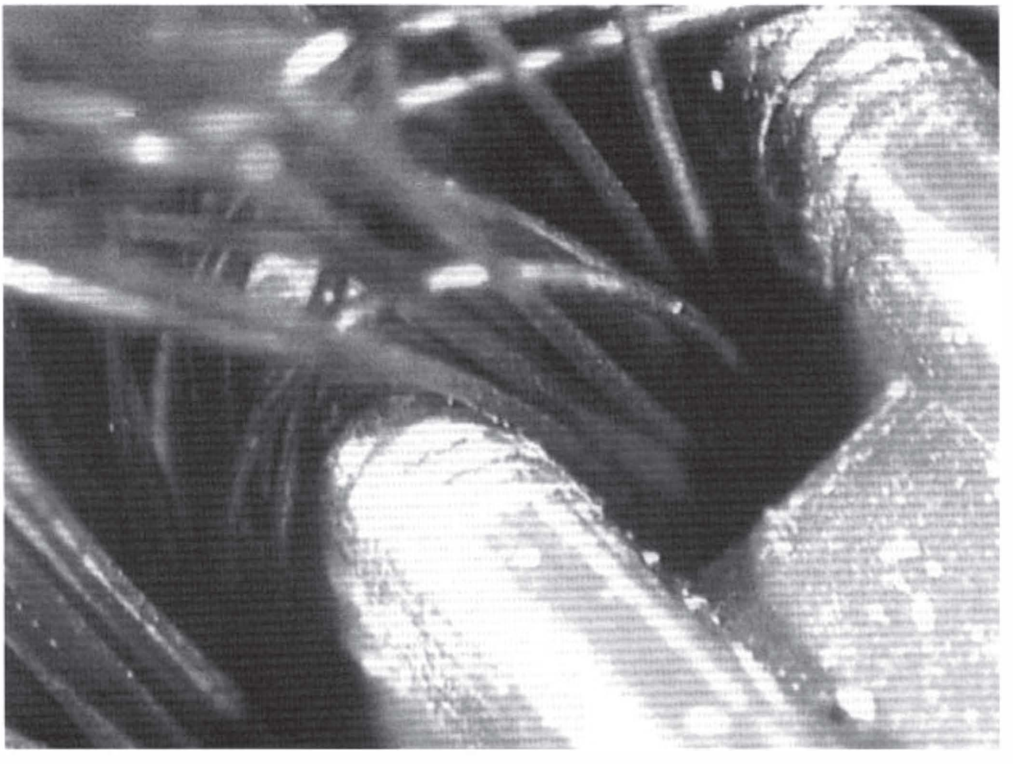


Figure 2. Dynamic bending of hair as comb is passed through tress.

polymer systems were tested for their ability to mend split ends. The experimentation evolved from testing individual polymers to polymer blends where it was discovered that a polyelectrolyte complex, formed between the ionic interactions of two oppositely charged polymers, provided positive effects in the mending process. The novel composition was found to have durability to a post combing treatment and was still able to be washed off the hair after a post shampoo treatment. Based on these features it was characterized as a semi-permanent hair repair effect. Besides a description of the polyelectrolyte complex used in this study, as well as test results, a proposed theory of the mechanism of mending is described. This mechanism serves as a model for designing other complexes that will have the same hair mending effect.

MATERIALS AND METHODS

MATERIALS

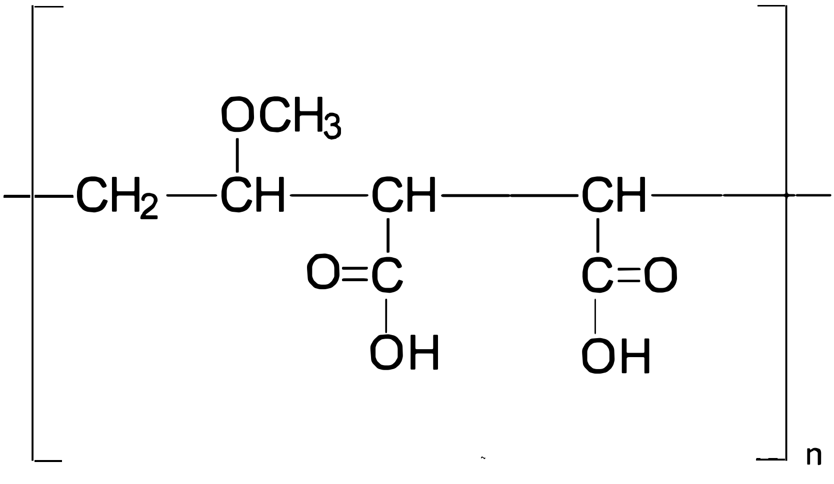
Natural brown hair tresses are supplied by International Hair Importers and are made with their patented swatching process to be 3.5 grams of loose hair, 6.5 inches in length from the bottom of the sewn end to the tip of the hair, and 1 3/4 inches across. Brand of combs used in the experiments are Sally's Beauty Supply. Fine teeth section of the comb contains eight teeth per centimeter.

The free acid form of the copolymer of methyl vinyl ether and maleic anhydride (INCI: PVM/MA Copolymer) is supplied by International Specialty Products under the trade name Gantrez® S-97 BF Polymer. The copolymer of vinyl pyrrolidone and methacrylamidopropyltrimethyl ammonium chloride (VP/MAPTAC Copolymer; INCI: Polyquaternium-28) is supplied by International Specialty Products under the trade name Conditioneze® NT-20. This is a 20% (w/w) solution in water. These ingredients are used as supplied and not purified or modified in any way. Figure 3 illustrates the structures of these compounds.

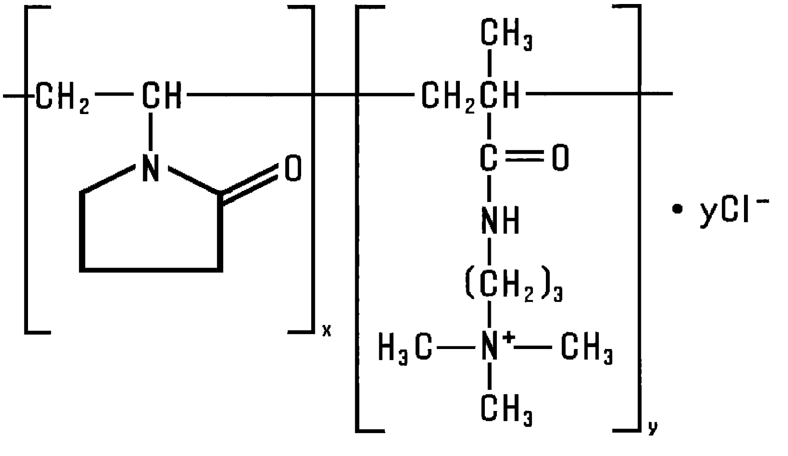
A commercial product with a split end mending claim was used as a benchmark. Its' ingredient label is: Aqua/Water, Cyclopentasiloxane, Propylene Glycol, Hydroxypropyl Guar, Phenoxyethanol, Peg 40 Hydrogenated Castor Oil, PEG/PPG-17/18 Dimethicone, Behentrimonium Chloride, Aminomethyl Propanol, Trideceth-12, Polyquaterium-4, Dimethiconol, Limonene, Linolool, Benzyl Salicylate, Amodimethicone, Alpha-Isomethyl Ionene, Perea Gratissima/Avocado Oil, Carbomer, Potato Starch Modified, Methyl Paraben, Butylphenyl Methylpropional, Citronellal, Cetrimonium Chloride, Laureth-23, Laureth-4, Prunus Armeniaca/Apricot Kernel Oil, Coumarin, Hexyl Cinnamol, Parfum/Fragrance, F.I.L. C1638713

EQUIPMENT

- Nikon SMZ 1500 Stereomicroscope
- Linksys 2.2 program for digital imagery (Linksys for Windows, Linkam Scientific Instruments Inc., 8 Epsom Downs Metro Center, Waterfield, Tadsworth, Surrey, KT205HT, U.K.)
- Thermal/Mechanical Styling Apparatus custom built at ISP to produce tresses with split ends.
- Amray model 1820/D digital Scanning Electron Microscope (SEM) with a LaB6



INCI: PVM/MA Copolymer



INCI: Polyquaternium-28, (VP/MAPTAC Copolymer)

Figure 3. Polymers used to form complex.

electron source, used to obtain high resolution images of fibers. The unit is capable of magnification up to 100,000×.

- Malvern Mastersizer S, used to measure particle size distribution of microgels of the complex in water. It determines particle size distribution of the liquid dispersions by using Mie laser light scattering theory. Mie theory, unlike Fraunhofer, allows consideration of particle refractive index, required for reliable results on particles <10 μm.

METHODS

Production of split ends on hair tresses with a thermal-mechanical apparatus. The hair obtained from International Hair Importers is essentially received undamaged. In order to start the experimentation, hair needs to be damaged to create split ends for repair. This is accomplished with a thermal/mechanical styling apparatus. This apparatus consists of two vent brushes that are attached to a cylindrical mixing blade. This is made to rotate with a mixer situated in a horizontal instead of its' normal vertical position. The mixer is adjusted so that it is made to rotate at 75 rpm against a hair tress. This treatment equates to approximately 9,000 brush strokes an hour. Simultaneously, the hair is subjected to the hot air of a blow dryer which is situated to keep the hair against the brushes during rotation. This treatment simulates what a consumer does during the styling process. This apparatus has been previously used for assessing the ameliorating effects of conditioning agents against the damage incurred by both thermal and mechanical stress (10). Prior to attaching the hair to the apparatus it is first dampened by rinsing for 10 seconds with warm tap water and combed through with a plastic comb to remove any snags. The hair tress is then put on the thermal/mechanical apparatus. The hair tress is subjected to this thermal/mechanical stress for 1.5 hours at 75 rpm. The hair blow dryer is set at warm and low fan and is pointed at the middle of the tress. The brush is set to a position to traverse at least ¾ of the tress length. At the end of the process, the hair tress is examined under low magnification to confirm that it is easy to find 20 split ends across the hair tress. If not, then more brushing is done until a satisfactory number of split ends are produced.

Pretreatment procedures. A split end fiber is isolated in the tress with the use of a magnifying glass and tweezers. The fiber is labeled at its root end. Split end fibers are chosen uniformly distributed throughout the tress. A dot is drawn with a red permanent marker slightly before the beginning of the split to later determine if the split broke off after combing. This procedure is repeated for 20 split ends for each tress. A total of five tresses are tagged in this way for a total of 100 fibers. This is the quantity of split ends for the study of one formula and provides a statistical basis for the results.

Pictures of each split end are taken under the stereomicroscope at 20×. The digital pictures for all of the 100 split end fibers are saved and their files are labeled as pretreatment. Data is tabulated in a chart as is illustrated in Table I. The following scoring system is used for future quantification of split end repair: end split = 1; no split = 0; partial split = 0.5.

The different degrees of splits are illustrated in Figure 4. First there is the major split which is termed primary. A split end within a split is termed secondary. Finer splits at the tertiary level are also observed at the 20× magnification. Each type of split is scored and tabulated in each step of the process. In this experiment only primary split end mending will be reported since this is observable with the naked eye and has the most effect on whole hair attributes.

Posttreatment and without subjecting the tress to combing. The tresses are first washed with 3% Ammonium Lauryl Sulfate solution for one minute and then rinsed well. The excess water is removed from the tress and 0.50 grams of the test composition is added to each tress and distributed uniformly with the help of combing. The tresses are then allowed to air dry. When the tresses are dry they are gently stroked to break any adhesion of the fibers from the effects of the treatment. As in the pretreatment step, pictures are again taken under the stereomicroscope for each of the 100 tagged fibers and their digital pictures are filed and designated as post treatment before combing. Split end mending assessment is again tabulated in the chart in Table I.

Table I
Tabulation of Data and Calculation of Mending for One Tress

Fiber#	Before treatment			After leave-on treatment (before combing)			After leave-on treatment (after combing)		
	P	S	T	P	S	T	P	S	T
1	1	0	1	0	0	0	1	0	0
2	1	0	0	0	0	0	0	0	0
3	1	0	0	0	0	0	0.5	0	0
4	1	1	0	0	0	0	0	0	0
5	1	2	1	0	0.5	0	1	0.5	0
6	1	0	0	0	0	0	0.5	0	0
7	1	1	0	0	0	0	0	0	0
8	1	0	0	0	0	0	0	0	0
9	1	0	0	0.5	0	0	0.5	0	0
10	1	0	0	0	0	0	0	0	0
11	1	0	0	0	0	0	0	0	0
12	1	1	0	0	0	0	0	0	0
13	1	1	0	0	0	0	1	0	0
14	1	1	1	0	0	0	0	0	0
15	1	0	0	0.5	0	0	1	0	0
16	1	0	0	0	0	0	0	0	0
17	1	0	0	0	0	0	0	0	0
18	1	0	0	0	0	0	1	0	0
19	1	0	0	0	0	0	1	0	0
20	1	0	0	0	0	0	1	0	0
Total split end	20	7	3	1	0.5	0	8.5	0.5	0
Complete mending (%)				90	85.7	100	50	85.7	100
Total mending (%)				95	92.8	100	57.5	92.8	100
Durability Index D							0.61	1	1

History of mending for each fiber as observed with stereomicroscope (1 = end split; 0 = intact end; 0.5 = partial split; P = primary split; S = secondary split; T = tertiary split).

Durability step—Posttreatment with combing the hair tress. Each hair tress is combed twenty times with the fine teeth of the comb. Pictures of the tagged fiber ends are again taken under the stereomicroscope and their files labeled as post treatment with combing. During the observation of each fiber the permanent mark is identified as a landmark to make sure the end of the split fiber has not broken off to guard against a false positive mending effect being recorded. Scoring is tabulated as before as is seen in Table I.

Calculation of split end mending percentage. The following two equations are used to calculate the degree of split end mending.

$$\text{Total mending } \% = \frac{\text{Total \# split ends before treatment} - \text{\# split ends after treatment}}{\text{Total \# split ends before treatment}} \times 100$$

Total percent mending includes the assessment of both complete and partial splits. Scoring: 1 = split end, 0 = mended split, 0.5 = partially mended split.

$$\text{Durability Index (D)} = \frac{\text{Total mending \% after combing}}{\text{Total mending \% before combing}}$$

Therefore, the maximum D = 1.0, and the minimum D = 0.

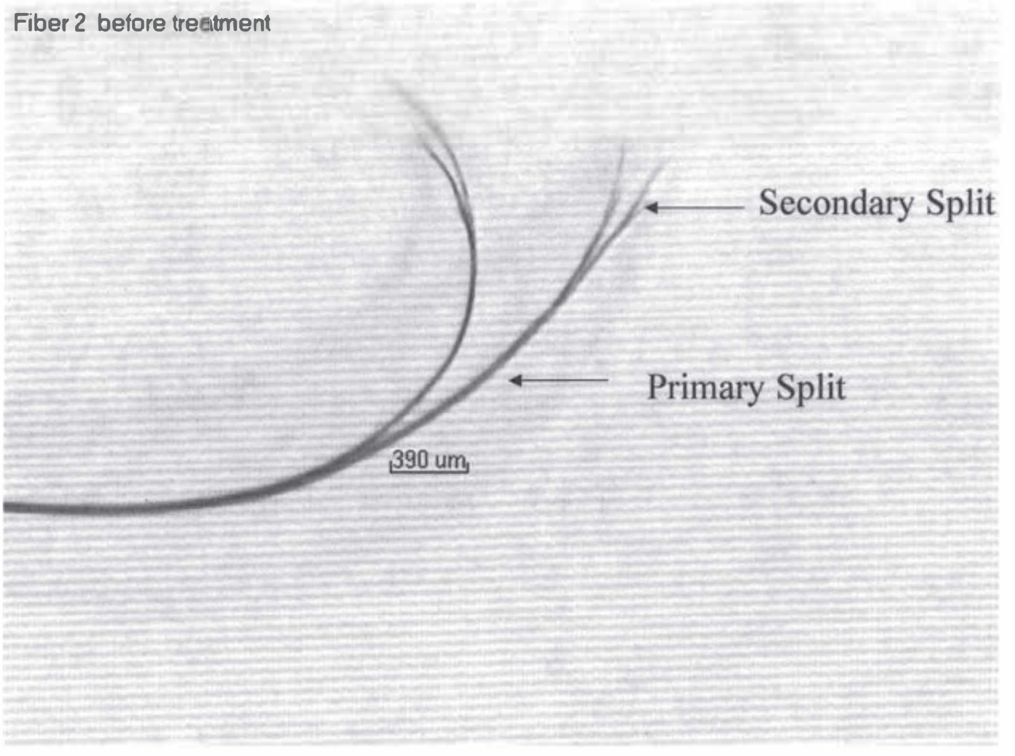


Figure 4. Stereomicroscopic view of fiber (20×) showing primary and secondary level splits.

All of the results reported in this study are based on total mending which includes the assessment of both complete and partial mending of the split end fiber. An example of the calculation of the tabulated data for one of the five tresses of a study is found at the bottom of Table I. Again, although the secondary and tertiary level splits are assessed as well more emphasis is placed on the primary splits since these are apparent to the naked eye and their mending would afford a consumer perceivable benefit.

Illustration of complete and partial mending. Figure 5 shows the three stages of the measurement cycle namely pretreatment, post treatment before combing, and finally post treatment after combing. The last step tests the durability of the mend. The red dot made with the permanent marker can be observed just prior to the split end. This series of photos in Figure 5A) serves to exemplify complete mending of the split end. Figure 5B) shows an example where the fiber has been partially mended after treatment and stays partially mended after the post combing process. In this case a score of 0.5 would be assigned. Both complete and partial mending are taken into consideration in the assessment of mending and is designated as total mending.

Advantages of the test method. Since the tagged split end fibers are part of the trees, application of the treatment can be performed in a realistic fashion simulating consumer usage. In this experiment the product is applied to damp hair and allowed to air dry. However, the method allows the study of different application techniques such as brush and blow drying or adding the treatment to dry hair for example.

The advantage of the tagging process allows the study of the fate of the split end after

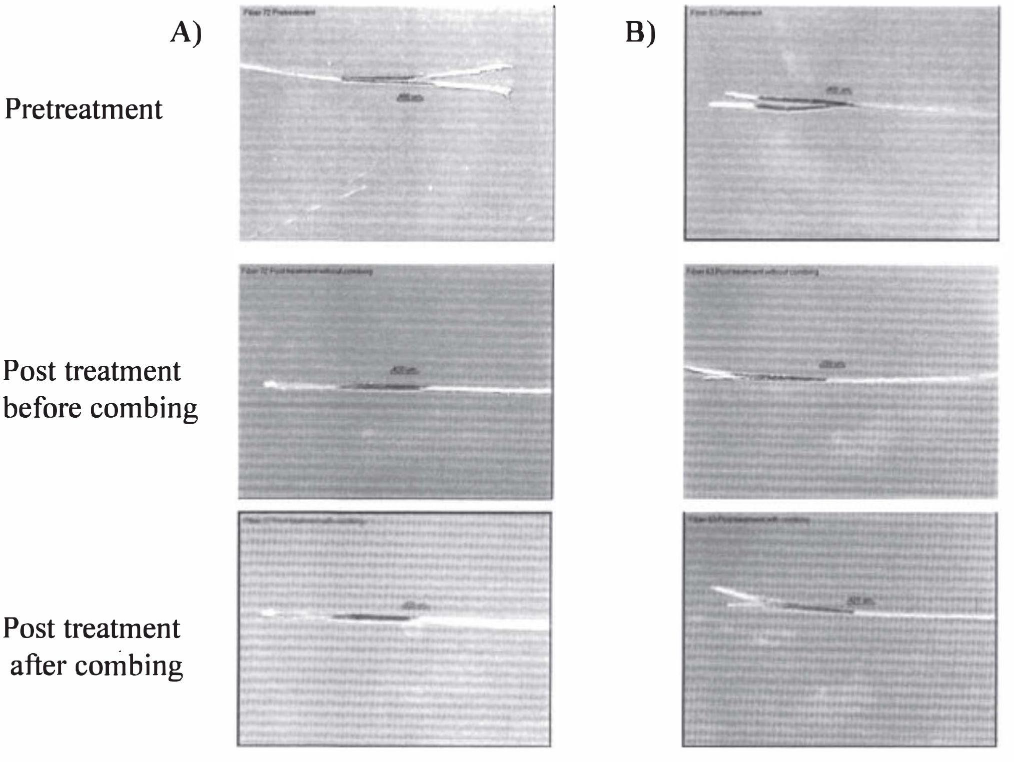


Figure 5. Examples of the two types of mending through the three stages of measurement: (A) Complete mending: split end is completely mended from start of fissure to end of fiber. (B) Partial mending: split end is mended from start of fissure to a fraction of the length to the end of the fiber.

treatment and more importantly to durability to combing. Since the fiber is still part of the tress it can be subjected to normal combing forces or other treatments to determine the effectiveness of the split end mending product. In this case the tress is subjected to twenty combings after application of the formulation. Combing was chosen to test durability since, as described above, the major cause of split end formation is through the shear stresses generated during the combing process. Also, the tagging process allows the study of other treatment variables such as survivability after washing, the effect of multiple treatments, or some other regimen designed by the experimenter to test split end mending durability.

Another advantage to the method is the increase in the depth of field that the stereomicroscope possesses over the optical microscope. As can be seen in Figure 4, the whole fiber end can be focused and observed under low magnification. In the figure it can be observed that this split end has a major bifurcation which is termed primary, and two minor splits which are termed secondary. The stereomicroscope also allows the observation of the fiber unhampered by a cover slip which may depress the fiber to the point where the split end will close. A slight shadow can be observed from the light source above the specimen showing that the fiber is not laying flat on the stage.

PRODUCTION OF POLYELECTROLYTE COMPLEX

Table II comprises the formulation used in the test. Test formulas utilize the complex

Table II
Formation of Complex and Formulation of Split End Mending Serum (61B)

Ingredients	%w/w
Phase A	
Deionized water	49.00
Xanthan gum (Rhodicare T)	0.50
Phase B	
Deionized water	36.00
Polyquaternium-28 **(conditioneze® NT-20)**	9.00 (1.80 active)
Phase C	
Deionized water	4.24
Sodium hydroxide (10% Aq. Soln.)	0.56
PVM/MA copolymer **(Gantrez® S-97 BF Polymer)**	0.20
Propylene glycol (and) diazolidinyl urea (and) iodopropynyl butylcarbamate **(Liquid Germall® Plus)**	0.50
	100.00%

Percent active complex = 2.00%.
Ratio of PVM/MA copolymer to Polyquaternium-28 = 0.20:1.80.

at 2 percent active with a ratio of PVM/MA Copolymer to Polyquaternim-28 of 0.20 to 1.80 respectively. The procedure for putting the full formula together (61B) which includes the production of the complex is as follows.

Procedure for full formula

1. In main container disperse Xanthan Gum into room temperature water with moderate propeller agitation. When fully incorporated switch to moderate sweep agitation and mix until uniform.
2. Add water of phase B in a premix container and mix with moderate propeller agitation. Add Polyquaternium-28 (Conditioneze NT-20) and mix until uniform.
3. Add water of phase C to a separate premix container and mix with moderate propeller agitation. Add sodium hydroxide solution and mix until uniform. Sprinkle PVM/MA Copolymer (Gantrez S-97 BF Polymer) into vortex and mix until uniform. Adjust pH to 6.95 ± 0.05 with sodium hydroxide solution.
4. Increase agitation of contents of phase B (~1000 rpm). Add phase C to phase B over the course of 20–30 seconds. Mix with fast propeller agitation for ten minutes.
5. Add combined phases B and C to phase A. Mix until uniform.
6. Dissolve preservative and mix until uniform.
7. Adjust pH to 7.1 ± 0.1 with 10% citric acid solution.

It is important to add the anionic polymer to the cationic polymer when forming the complex. Also, the complex should be made prior to its incorporation into a formulation; the steps in the above procedure for making the complex are 2 through 4. When incorporating the complex into a formula the integrity of the complex is judged microscopically to determine if it has a typical microgel structure which is described below. This is a predictive indicator for the efficacy of the complex to repair split ends. The complex has shown to be compatible with nonionic and mildly cationic and anionic polymers. In this case the complex is added to the anionic polymer Xanthan Gum to make a serum product. One of the control formulas is made by adding the complex alone to water to obtain two percent active.

RESULTS AND DISCUSSION

FORMATION AND CHARACTERIZATION OF POLYELECTROLYTE MICROGEL COMPLEX

There have been various names for polyelectrolyte complexes. These consist of such names as polymer-polymer complexes, or interpolyelectrolyte complexes. Despite their nomenclature as used in the academic literature they are described as two species of polymers that can interact with each other without the formation of covalent bonds. The bonds involved could be electrostatic, hydrogen bonding, Van der Waals interactions, or a combination of each. The polyelectrolyte complex used in this study is based on the electrostatic interactions of two oppositely charged molecules. It is not just a mixture of two polymers. As can be seen in Figure 6 high molecular weight linear polyanionic and polycationic polymers when combined together form a complex through the association of their opposite charges (12). There are numerous factors that should be briefly mentioned at this point that are important in the formation of the complex. Besides considering the weight ratios of the two unlike charged polymers other factors involved in the interaction are molecular weights, charge densities, pH and electrolyte content of the solvent, the solvent type, and the process of putting the two polymers together. Since unlike charges interact on a molar basis, the stoichiometry and charge ratios are important in considering their interaction.

The hypothesis was that split end mending can be achieved with a polyelectrolyte complex made through the interaction of two oppositely charged polymers. This is in distinction to split end mending with a polymer-surfactant complex as patented by Ramashandran et al. (13). They invented an ingenious hair rinse composition that claimed would not only condition hair to provide such properties as wet detangling, but also lend fixative properties and repair split ends. The three main ingredients that comprised the rinse are quaternary ammonium salts (quat), water insoluble acrylic or acrylate polymers and a solvent that comprises a long chain alcohol and/or alcohol ethoxylate. The solvent is used to help compatibilize the quat and polymer. It was theorized that the quat and polymer form a complex with each other in the solvent and

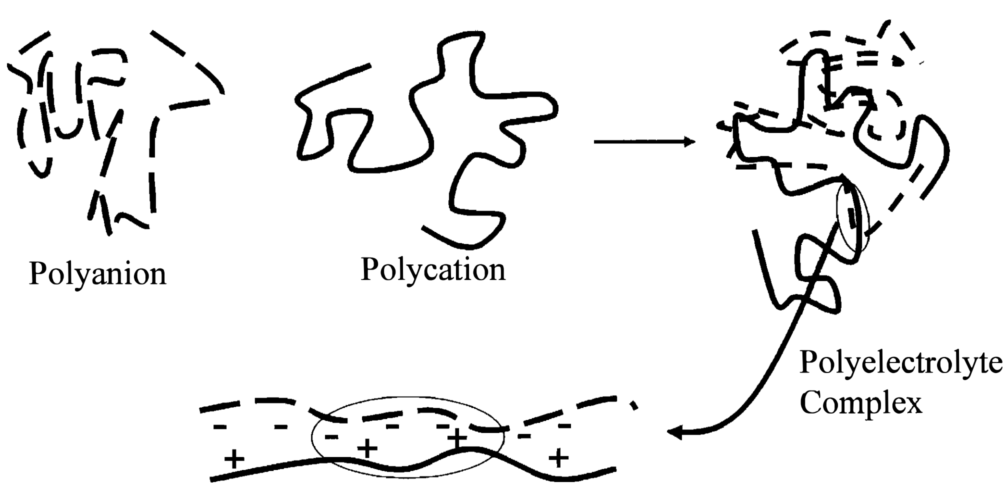


Figure 6. Ionic association of polyelectrolytes of different charge that forms a complex; adapted from reference (12).

aids the deposition of the anionic polymer on the hair during the rinse cycle which would otherwise be washed away. They also theorize that split end mending is achieved by the adhesiveness of the deposited polymer which when dried forms a film that holds the splits together.

Using the specialized test method as described in the methods section above allowed the screening of many types of compositions which led to the formation of the hypothesis. Some individual polymers or mixtures of polymers gave only a poor to fair mending durability efficacy. The composition discovered based on a polyelectrolyte complex was found to have increased/mending durability efficacy over control systems. The anionic polymer of this complex is PVM/MA Copolymer. The anionic contribution of this molecule depends on pH since it has two carboxylic groups per monomer unit. The cationic polymer component is Polyquaternium-28 or VP/MAPTAC Copolymer. Its cationicity is from the quaternary groups and are positively charged despite pH. The electrostatic interaction then is between the ionized carboxylic group of the anionic polymer and the quaternary nitrogen group of the cationic polymer (14).

When the complex forms it can be characterized microscopically as a microgel structure. Figure 7 shows the characteristics of these microgels based on the polyelectrolyte complex as observed under an optical microscope at 500×. It can be observed that these particles are translucent, non-uniform in shape, and are dispersible in the aqueous

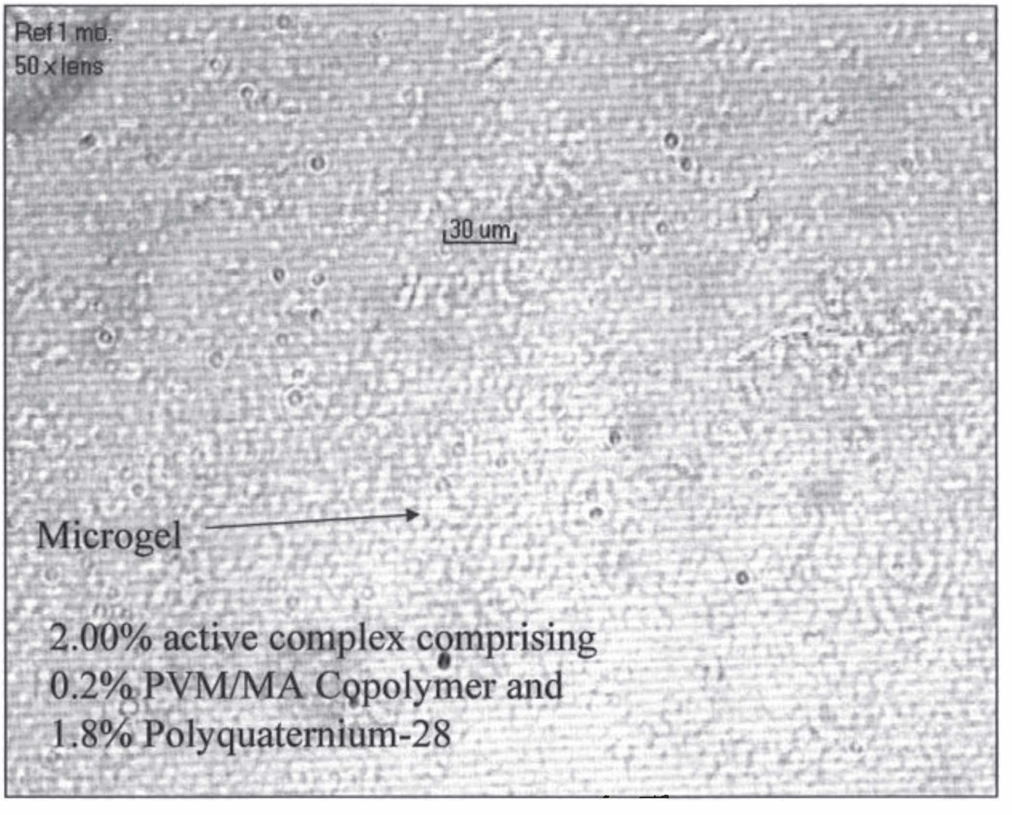


Figure 7. Microgel structure as observed under optical microscope (500×)

solvent. Stability shows that a 4% active complex dispersion is stable at elevated temperatures and multiple freeze thaw cycles. The particles are in the range of 5–10 microns in size as measured with a Malvern particle size analyzer. The particle size distribution is illustrated in Figure 8.

By studying the phase diagram formed between PVM/MA Copolymer and Polyquaternium-28 the phase regions of their interactions were identified. In building this phase diagram various weight ratios were used in putting the two polymers together while keeping other variables constant. The variables kept constant were the solvent which was water, pH of the PVM/MA Copolymer which was adjusted to 7.00 ± 0.05, and the type of polymer which inherently controls the molecular weight and other intrinsic properties of the polymers such as cationic charge density. The process of putting the two polymers together was also kept constant. The character of the polymer combinations were noted and given a value against set criteria. The phase diagram was produced by regression analysis with the help of statistical software (15). The resultant phase diagram is illustrated in Figure 9. The complexes were characterized macroscopically by appearance where the value of 5 was given to clear solutions, 1 was given to opaque white dispersions, and 2 through 4 for intermediate values for solution characters; see legend in Figure 9. It was first thought that the opaque milky white dispersions designated 1 only

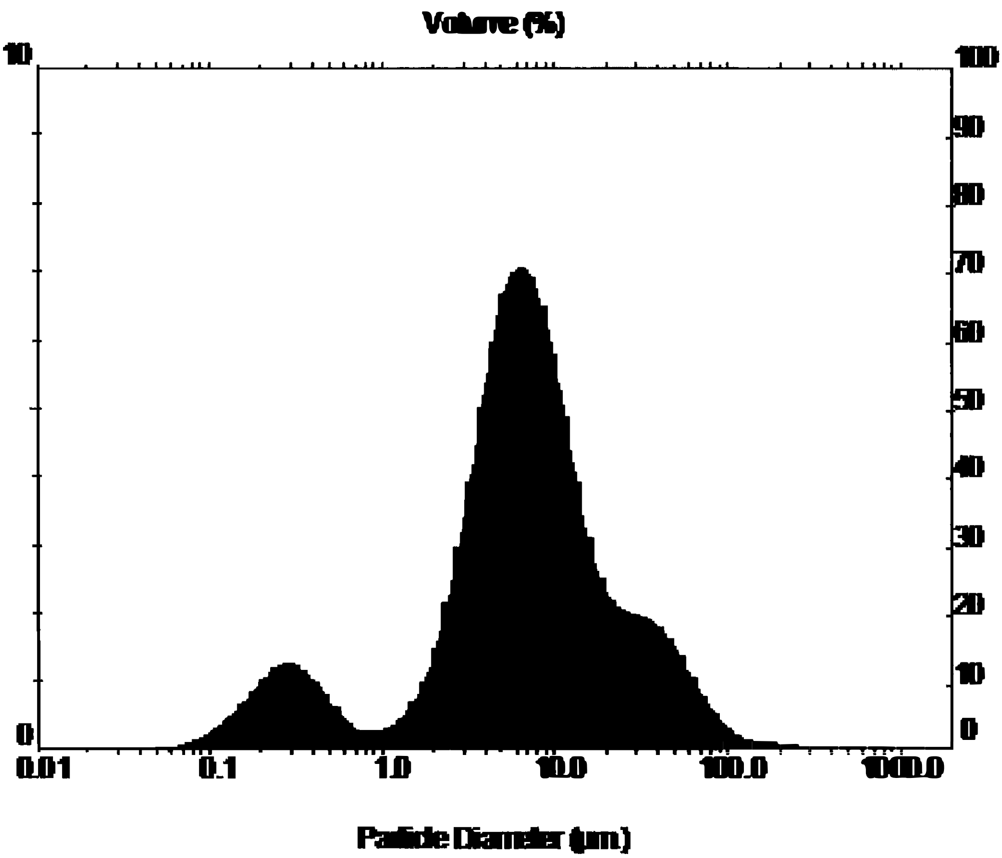


Figure 8. Malvern particle size analysis of microgel structure.

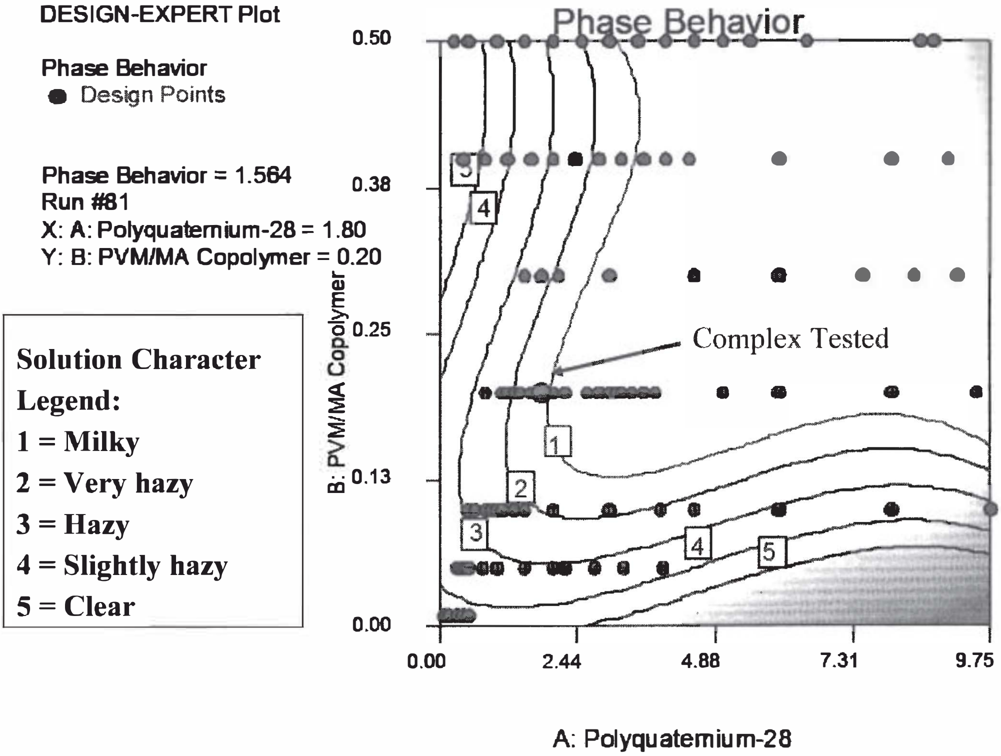


Figure 9. Phase behavior of polymers of differing charge.

contained the complex, but with further investigation under the microscope it was observed that all dispersions other than the clear ones contained microgels. It was concluded that the white opaque dispersions then had the highest intensity of microgels formed and would be most appropriate for testing the split end mending benefit. The complex tested in this study is identified in Figure 9 and consists of two percent active complex made by combining PVM/MA Copolymer and Polyquaternium-28 at a weight ratio of 0.2 to 1.8 respectively.

Polyelectrolyte complexes based on other anionic and cationic polymer combinations were studied in this way but have not been tested for mending efficacy. Complexes using PVM/MA Copolymer as the anionic component have been formed with Polyquaternium-7, 10, and 11. Also, Vinylpyrrolidone/acrylates/laurylmethacrylate copolymer serving as the anionic polymer has been complexed with Polyquaternium-28.

The phase diagram built in Figure 9 is based on weight ratios of the two polymers. However, the two polymers are actually interacting on a stoichiometric basis through their charge interaction. To further elucidate the interaction of these two polymers the following study was conducted and is illustrated in Figure 10. Various levels on a weight basis of Polyquaternium-28 were combined with 0.2% PVM/MA Copolymer. The resultant viscosity was measured using a Brookfield viscometer with a small sample adapter and the viscosity plotted against the calculated mole ratio of cationic monomer to anionic monomer. The shape of the curve is distinctly parabolically curved containing a minimum viscosity. It was discovered that this minimum of viscosity occurs at a

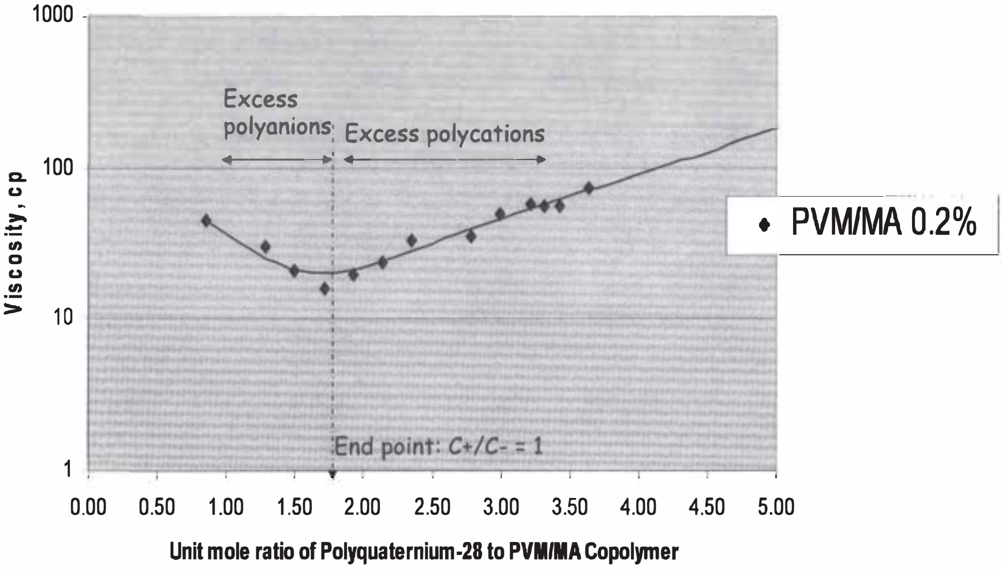


Figure 10. Dependence of viscosity on unit mole ratio cationic to anionic groups.

stoichiometric charge ratio of one to one where the stoichiometric equivalence of cationic and anionic charges are the same. This indicated a maximum in the amount of microgels formed since these are discrete particles that are dispersed in solution. Polymer ratios deviating away from the one to one stoichiometric equivalence would contain polymer not associated in a microgel and would increase the viscosity of the solution. The lower viscosity evident for the 1:1 ratio was due to the hydrodynamic volume of the complexed chains being smaller than when free un-complexed polymers are present in solution at other charge ratios. This charge-charge interaction contributes to the compact nature of the microgel structure of the complex and exemplified the stoichiometric interaction of the two polymers. It was determined that the complex chosen to repair split ends has a cationic to anionic charge ratio of precisely 1.14.

MENDING TEST RESULTS OF MICROGEL COMPOSITION

A screening study showed the efficacy of the polyelectrolyte complex in split end mending durability. The control systems were based on the component polymers of the complex used alone and a clear 1:1 mixture of the two polymers where there are no discrete microgels present. All polymer and polymer combinations were kept constant at a total of 2.00% active. This screening study consisted of measuring twenty tagged fibers for each formulation instead of the usual one hundred and was based on complete mending as observed with a magnifying glass. Test results showed that the complex had increased durability of mending over the control formulations. Test results are in Table III.

When the complex was used alone at 2.00% active in a one hundred fiber study it mended 92 out of 100 fibers after treatment and before combing. After combing the tress twenty times 68 fibers remained mended. When the 2.00% active complex was formulated into a simple lotion formula thickened with Xanthan Gum approximately

Table III
Screening Experiment Showing Efficacy of Complex Over Systems Used as Controls

Formula type	% Mending after treatment	% Mending after combing	Durability index
2.00% neutralized PVM/MA copolymer	90	15	0.17
2.00% Polyquaternium-28	75	40	0.53
2% Complex; 0.20 neutralized PVM/MA copolymer and 1.80 polyquaternium-28	90	75	0.83
1.00% neutralized PVM/MA copolymer plus 1.00% polyquaternium-28	85	20	0.24

the same results were obtained. This provided evidence for two things. First, that the results were reproducible giving validity to the test method. Second, the complex could be formulated into a system without loss of efficacy. Results are portrayed in Figure 11. In both cases the durability indices of the mending after combing was over 70%.

As mentioned in the procedure there are 100 fibers tested for each treatment, twenty fibers tagged on one tress times five tresses. The data illustrated in Figure 12 shows the variability of mending for each tress for both before and after combing on the full formulation. The average and standard deviation of the mending results after combing of the five tresses is 67.6 ± 12.6%. Comparing this mending data to a control formula containing just the thickening agent as can be seen in Figure 13 shows the significance of the difference. From this it can be concluded that the complex is responsible for the high mending scores.

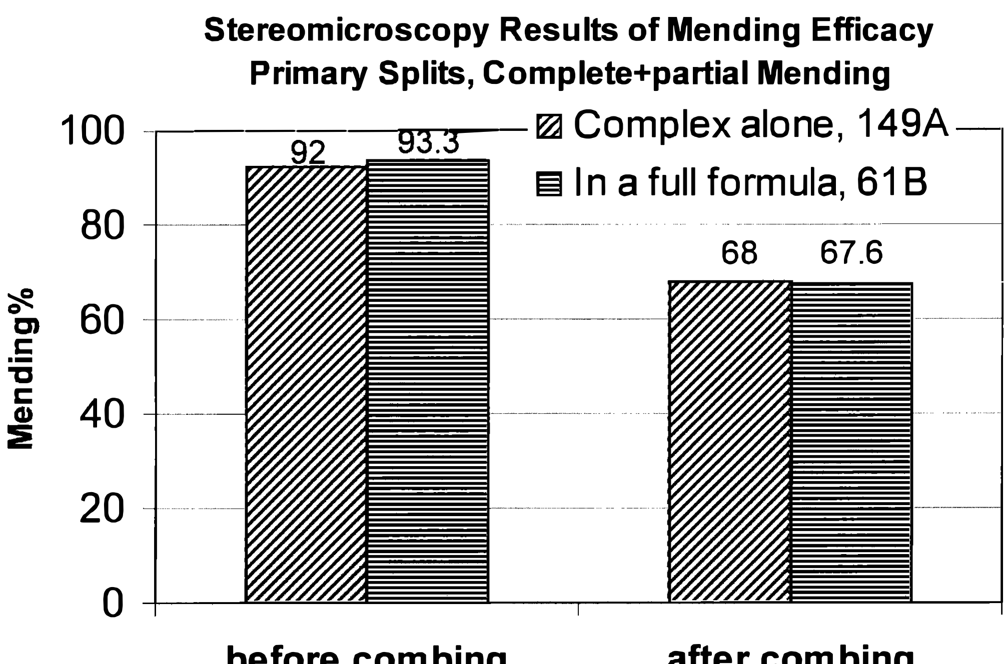


Figure 11. Total percent mending of complex alone and in a framework formula both before and after combing.

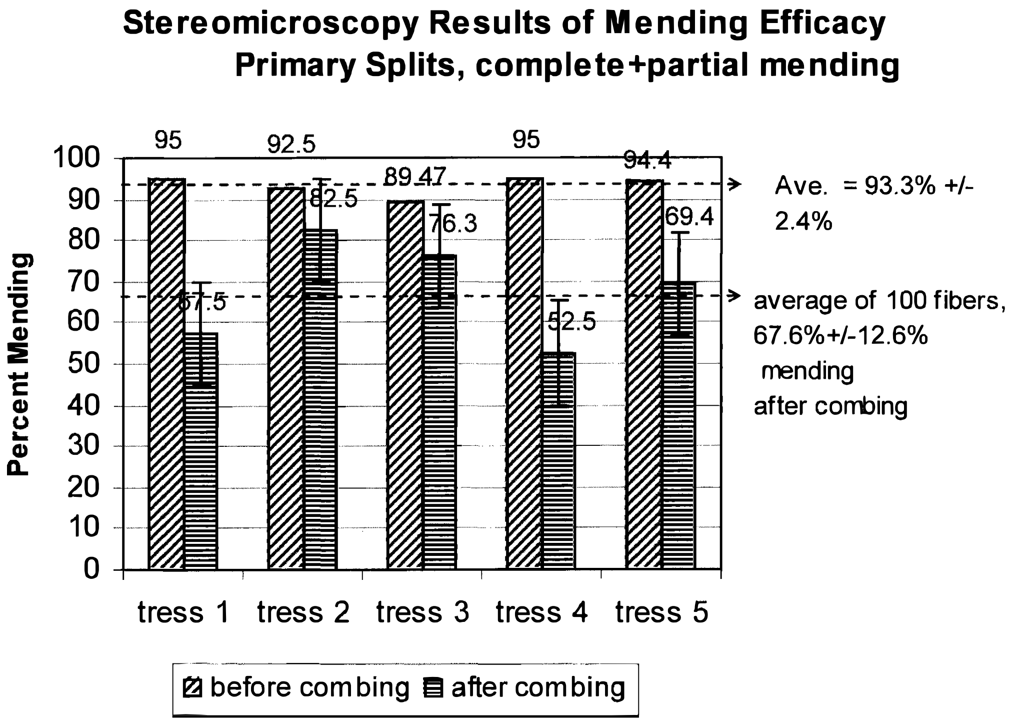


Figure 12. Variance of mending efficacy for five tresses used in one experiment.

Complexes based on different weight ratios of cationic to anionic polymer were tested for split end mending efficacy. It was discovered that although there were microgels formed by the interaction of Polyquaternium-28 and PVM/MA Copolymer, an optimal amount of repair was evident when the two polymers were combined when their charge ratios were 1:1 as can be seen in Figure 14. Split end mending efficacy is reduced as the polymer ratio deviates from the one to one charge ratio. This is further evidence in showing the importance of the polyelectrolyte complex in mending split ends.

The advantage of the developed method is to determine the fate of the split ends through various treatments that test the durability of the mend. Since the tagged split end fiber is always part of a tress it can be treated in such a way that it is exposed to realistic treatments. In the previous case the tress was subjected to a controlled amount of combing to test the durability of the mend. Other treatment regimens can be conceived to test durability in a realistic fashion. A test was devised to determine the effect of multiple treatments of the formula with the complex and its removability with shampoo. One cycle consisted of treatment with the formula, drying, combing, and then washing. Split end mending was assessed after treatment before combing, after treatment after combing, and finally after washing for one, two and five cycles of the treatment schedule. Results of the test are illustrated in Figure 15. First it can be observed that mending is high after treatment but before combing for treatment cycle one through five. Durability to combing stress over the multiple treatment cycles stays the same and is approximately 60%. Durability to washing is low and decreases with continued use. It was observed during the mending tabulation that the split ends became more severe with continued washing which explains the lowering of the percent mend-

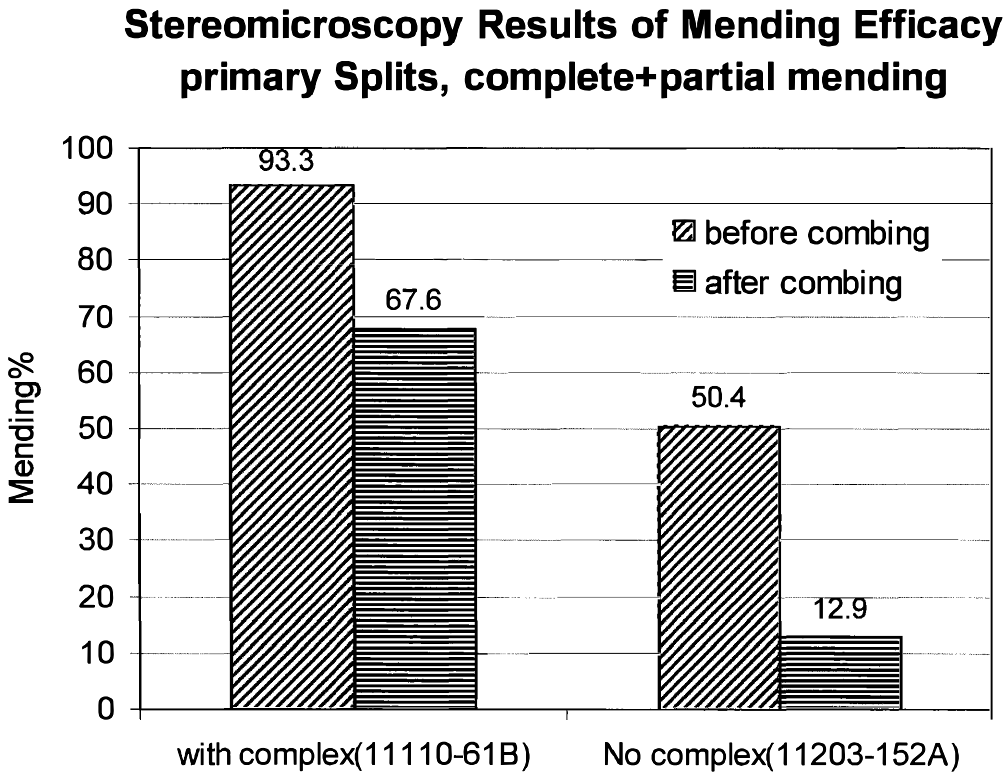


Figure 13. Total percent mending of formula with complex vs control.

ing scores after multiple wash cycles. Measurements taken before and after treatment after one cycle are approximately the same as the previous data and show again the reproducibility of the data. The implications of these conclusions related to consumer performance include that the product can be claimed that it will not have the negative effects of build up with continued use and that product directions should include adding the product to the hair after every shampoo in order to obtain the desired effect.

There are few commercially available products on the market that claim split end mending. The one found was tested as a benchmark for performance to the formula with the polyelectrolyte complex. Although the commercial product was able to mend split ends initially after treatment, the mends failed after post combing. Total percent mending is considerably lower after combing for the commercial product vs. the formula with the polyelectrolyte complex (Figure 16A). Durability index of the commercial product is much lower especially for primary split ends (Figure 16B). The mechanism responsible for temporarily mending split ends in the commercial product is probably through a lowering of the surface energy of the fibers after treatment. The damaged parts of the fibers are then attracted through weak hydrophobic bonds. Ingredients responsible for this are the blend of silicones in the product such as cyclopentasiloxane, dimethicone, alkyl modified dimethicone, dimethiconol, and amodimethicone. Other ingredients having the same effect are the cationic surfactants and organic oils; refer to methods section for ingredient labeling. This hydrophobic mechanism, although it provides a high degree of mending, fails to provide durability to the mend as exemplified in the

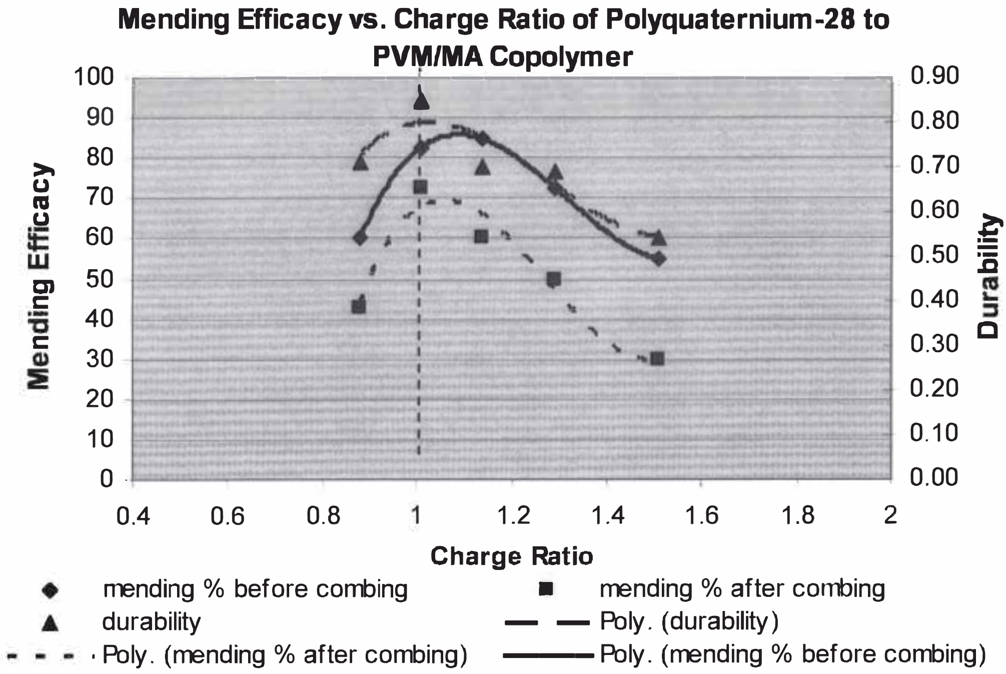


Figure 14. Mending efficacy vs charge ratio of cationic to anionic polymer.

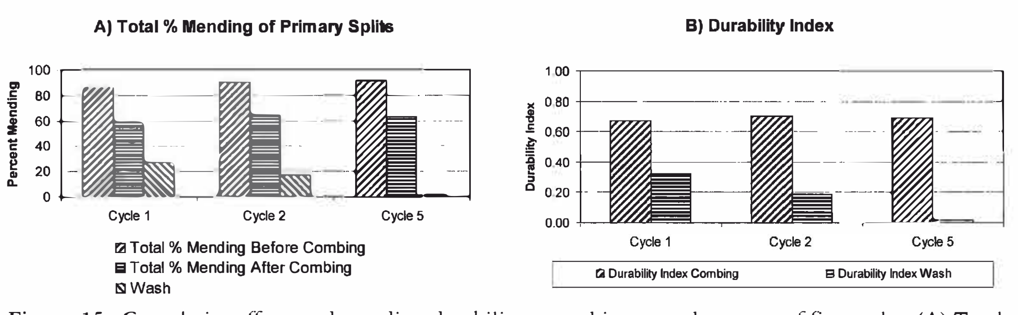


Figure 15. Cumulative effects and mending durability to washing over the course of five cycles. (A) Total percent mending of primary splits. (B) Durability index.

post combing durability test. The hydrophobic bonding of the components of the split fiber is not strong enough to withstand the stress of the combing process.

In our screening experiments for the polyelectrolyte complex it was found that there were many compounds that could mend split ends prior to stressing the tress to test the durability of the mend. It was the ability of the complex to durably mend the split ends after this post combing process that provides this semi-permanent mending ability. Based on the surface characteristics of damaged hair as well as the structure and chemical interactions of the polyelectrolyte complex with hair, a theory was proposed on the possible mechanism of this semi-permanent split end mending.

PROPOSED THEORY OF SPLIT END MENDING

Hydrophilic character of damaged hair. Human hair consists of a central core called the

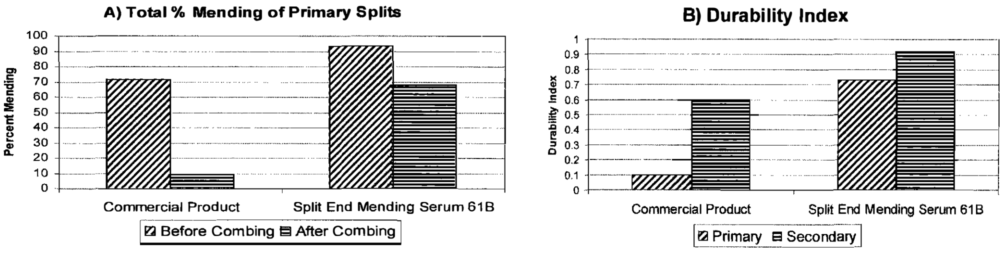


Figure 16. Comparison of mending with complex vs a commercial product. (A) Total percent mending of primary splits. (B) Durability index.

cortex covered by a sheath of several layers of flattened cuticle cells. Each of these overlapping scales is about half micron thick and 45 microns long. The thin outermost layer that forms a sheath around the cuticle cell is known as the epicuticle and is hydrophobic, whereas, the cortex is hydrophilic (16). The outer layer of cuticle surface contains 18-methyleicosanoic acid (18-MEA) also called the F-layer, which makes the hair surface hydrophobic. 18-MEA binds with the A-layer containing cystine groups in the cuticle cell. The main function of the cuticle is to provide mechanical protection for substances inside the cortex layer such as preventing amino acid and proteins from washing out through the hair surface or protecting it from further damage. When hair becomes damaged there are both physical and chemical changes to both the surface and internal structures of the hair fiber. The morphological changes of a damaged hair fiber are evident as illustrated in Figure 17. Besides the obvious split in the fiber exposing the subassemblies of the cortex it can be observed that the cuticle is partially lifted as well. For a damaged hair fiber containing a split end, as shown in the SEM picture, the cuticle layers are chemically damaged as well resulting in the hair fiber being more hydrophilic. This might be due to the exposure of the cortex after cuticle damage and/or the exposure of the A-layer in cuticle cells. The A-layer contains high level of cystine groups (>30%). The disulfide bond in cystine, -R-S-S-R-, is very reactive and is in a state to be oxidized. One of the possible oxidation products of cystine is cysteic acid, R-SO_3^-. When the F layer is stripped the increased levels of cysteic acid on the damaged hair surface will contribute to its increased hydrophilicity.

A simple test demonstrates that damaged hair is more hydrophilic than undamaged hair. A hair tip with a split end and a healthy hair tip were soaked in a 0.03% cationic dye solution called Safranin used in microbiological staining for 30 seconds and rinsed in running water. The hair fibers were then observed under a stereomicroscope. The microscope image in Figure 18 shows that the split tip end turns to a much more red color than the healthy hair. This is due to the higher interaction of the cationic stain with the increased number of anionic sites of the damaged fiber which are due to the chemical and morphological changes in the hair surface. The positive response to staining indicates that the hair surface or cuticle cells are damaged after the hair fiber splits and is consistent with the SEM results in Figure 17 which shows the cuticle damage characterized by jagged edges.

Besides the staining test there have been many studies that show that the hair surface becomes more hydrophilic or more negatively charged when damaged. For example, it has been reported that the hair surface becomes hydrophilic because of the exposure of uncovered A-layer after exfoliation of hydrophobic F-layer by the action of hydrogen

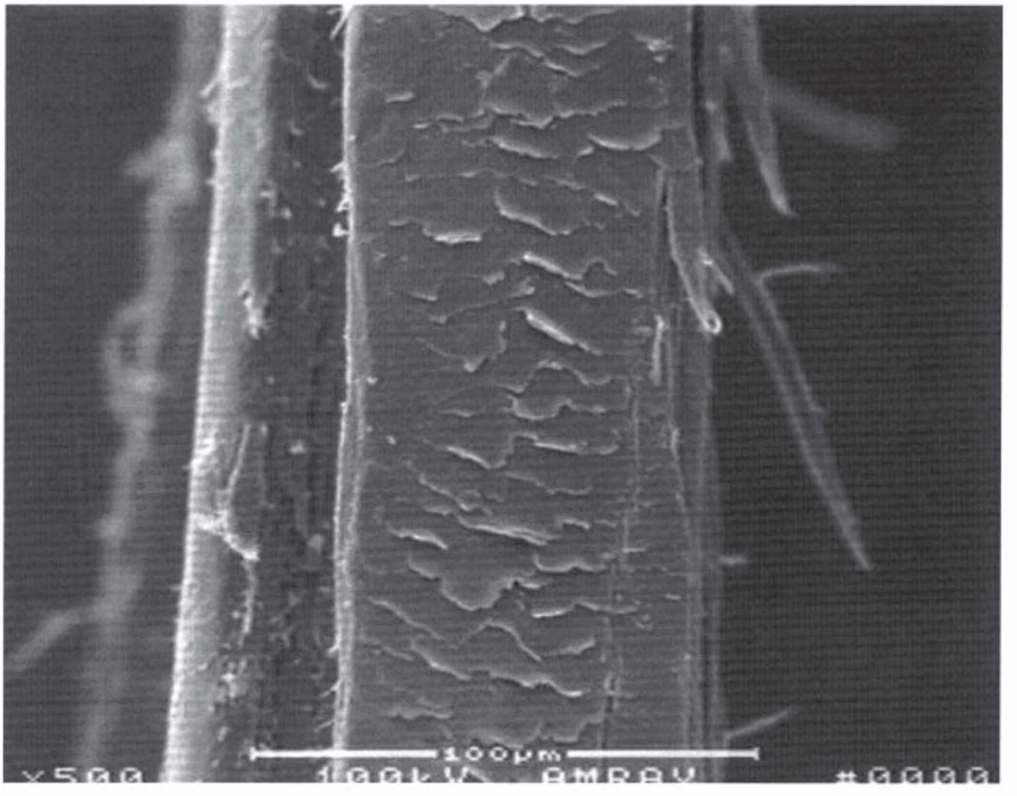


Figure 17. SEM showing split end and cuticle lifting.

peroxide and alkali used in hair coloring (17). Ruetsch found that when hair is subjected to chemical oxidation that a positive response is obtained by treatment with the cationic fluorochrom, Rhodamine B (18). Also, the dye response was found to be directly proportional to the treatment time. Cysteic acid was revealed to be the new species on the surface of the hair based on chemical analysis through X-Ray photoelectron spectroscopy.

FTIR has been shown to have utility in measuring the hydrophilic nature of damaged hair (8). The disulfide bond when oxidized by a damaging process can be detected by the shifting bands in the IR spectrum as the chemical functional groups change to more hydrophilic species. The oxidation products formed in hair depend on the nature of the oxidizing agent. Joy et al. reported that when hair is treated with alkaline hydrogen peroxide solutions the IR peak at approximately $1040 cm^{-1}$ corresponding to cyteic acid is significantly changed confirming disulfide oxidation (19). It was also found in the study by Joy that cysteic acid content increases from root to tip end of both naturally weathered and bleached hair showing the increase of damage of the hair with age.

Another piece of evidence showing the increase in the hydrophilic character of the surface of damaged hair is an increase in surface energy. Through the use of the Wihelmy balance technique tested on single fibers, it was found that both oxidation and reduction increased the wettability of the hair (20, 21). They attribute these increases to again the generation of hydrophilic groups such as sulfonic acid groups in the case of oxidation and thiol groups in the case of reduction.

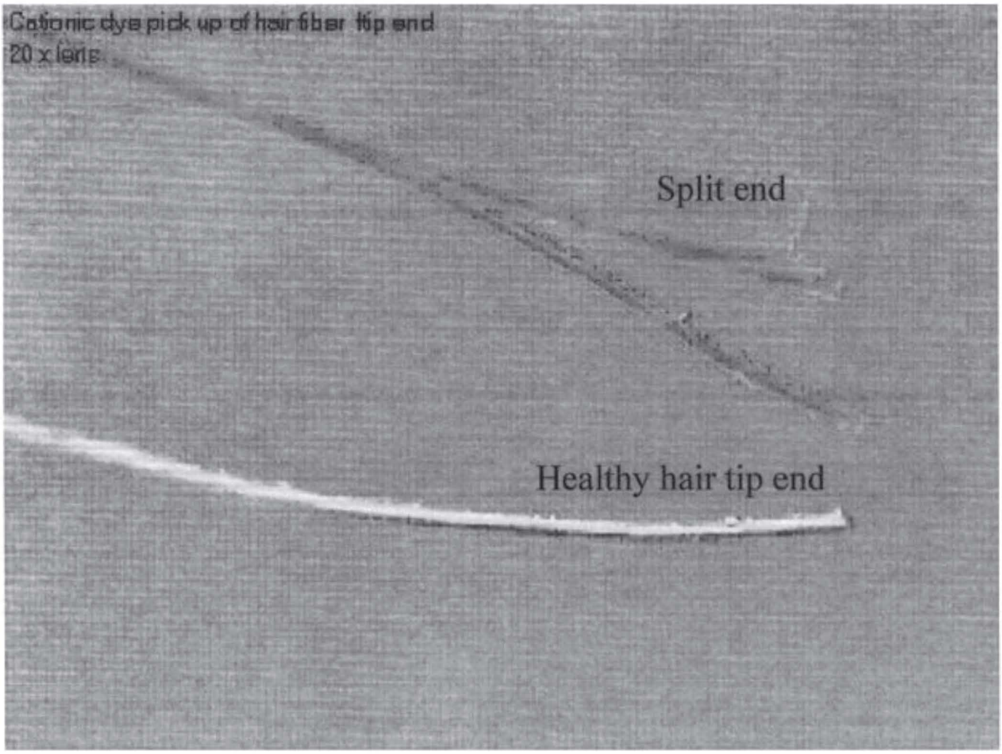


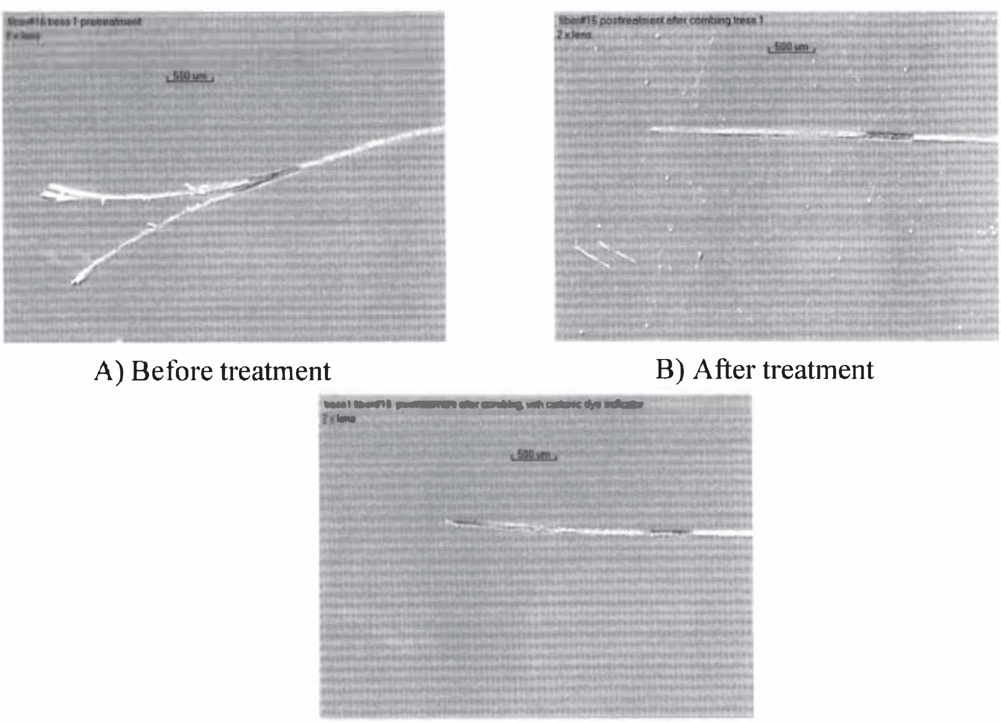
Figure 18. Ionic dye reaction to damaged hair.

Structure-property relationships are important factors to consider in the process of either choosing or designing ingredients to test for hair repair. One has to theorize how the ingredient will interact with the fine structure and chemistry of hair in order to determine if it is a candidate for experimentation. A few experiments have been shown in this paper that provides evidence that there are changes in the morphology and chemistry of hair during the damage process. One thing that is essential therefore in the repair process is that the ingredient has to have a cationic nature in order to bind to the anionic hair surface of the split fibers. Also, adhesive effects are necessary that are able to glue the split subassemblies of the fibers together. Lastly and most importantly the composition needs to be able to close the split ends and smooth the lifted cuticle scales so as to ensure a durable mend especially after combing or other stress factors during for example hair styling. Considering the chemistry and morphology of the microgel structure and its interaction with the chemistry and morphology of damaged hair, it seems reasonable that the polyelectrolyte complex is able to meet all of these criteria for the hair repair process. Based on this thinking a mechanism of action for the semi-permanent split end mending effect is proposed.

Proposed mechanism of split end mending with PEC microgel. It has been shown that maximum mending was achieved from microgels that were formed from polyelectrolyte complexes made from combinations of oppositely charged polymers close to a one to one stoichiometric charge ratio. This charge ratio was shown through viscosity measurements to be the point of maximum complexation. It is believed that although this charge ratio is balanced there exists in the microgel residual anionic and cationic charges that have not associated together. This is because of the steric hindrance that prevents the two macromolecules to completely associate all of their unlike charges together for complete neutralization.

There are various aspects to the proposed mechanism of action of the hair repair process with the polyelectrolyte complex. First, the residual cationic charges on the microgel would tend to bind to the anionic sites of the damaged cortex through electrostatic association. To show the cationicity of the complex the anionic dye, Direct Red 80, was used as an indicator. Figure 19 shows a split end before treatment with the complex, after treatment showing mending, and after treatment with Red 80 showing a positive response to the dye. The higher level of red towards the tip indicates the predominance of complex. The red mark just prior to the split end again is the mark made with a permanent marker.

During the drying stage the microgel complex is able to form a crosslinking structure which bridges the subassemblies of the fiber together. The microgel structure and its interaction with hair are illustrated in Figure 20A. The crosslinking adhesive structure of the microgel serves to glue the damaged parts of the fiber together. Since the complex is in the form of microgels in the size range of 5–10 microns they are small enough to infiltrate the fissures of the split cortex especially those as can be seen macroscopically as a split end. The smaller particles can to a certain extent permeate the lifted cuticle which is also present in damaged hair. After drying the microgels form a clear durable film which tends to bind these damaged parts of the hair together as is illustrated in



A) Before treatment

B) After treatment

C) After treatment plus Red 80

Figure 19. Anionic Direct Red 80 dye test indicates more microgel deposition on tip end.

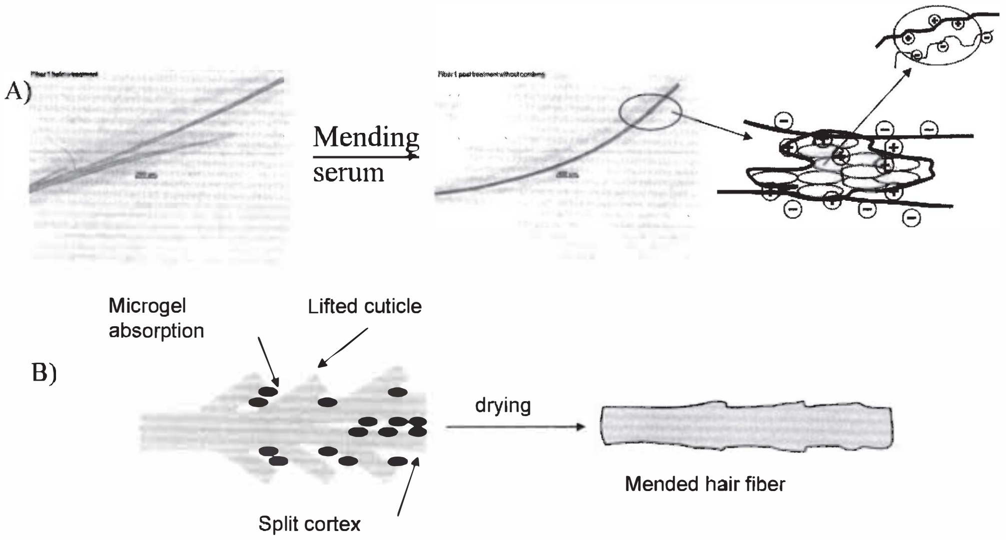


Figure 20. Proposed mechanism of split end mending. (A) Microgel crosslinking structure. (B) Binding of cuticle and split end during the drying process.

Figure 20B. The unique features of the dried thin film ensure a durable mend that will survive the combing process. These various aspects of the mending mechanism provides for an efficacious level of mending that can endure a post combing process which is typical of normal styling behavior. Visual effects of this mending can be observed through SEM. In Figure 21 it can be observed that the mended fiber has a smooth cuticle where before treatment it was characterized as lifted. Also, the seam of the weld is evident where the split end used to be.

Having an increased understanding of the formation and chemistry of polyelectrolyte complexes and their interaction with the chemistry and morphology of hair allows the design of new compositions that could function in the same way as the complex studied here.

CONCLUSIONS

Hair styling trends have created a need for hair repair compositions that will attempt to restore damaged hair to its normal state. Split ends are one manifestation of that damage. A test method has been devised that can assess in a realistic fashion the mending of split ends through various treatment regimens. The method is realistic in that the tagged split end fibers are part of a tress that can be subjected to normal combing or washing cycles. With this method it has been discovered that a polyelectrolyte complex can semi-permanently mend split ends in that split end hair treated with this composition can survive the stress of combing. The composition is efficacious especially in comparison to a commercial benchmark with a split end mending claim. A proposed mechanism of action has been put forth and consists of the microgel structure of the polyelectrolyte complex acting as a crosslinking structure in the damaged subassemblies of the damaged fiber. The understanding of this mechanism opens the way for the development of new

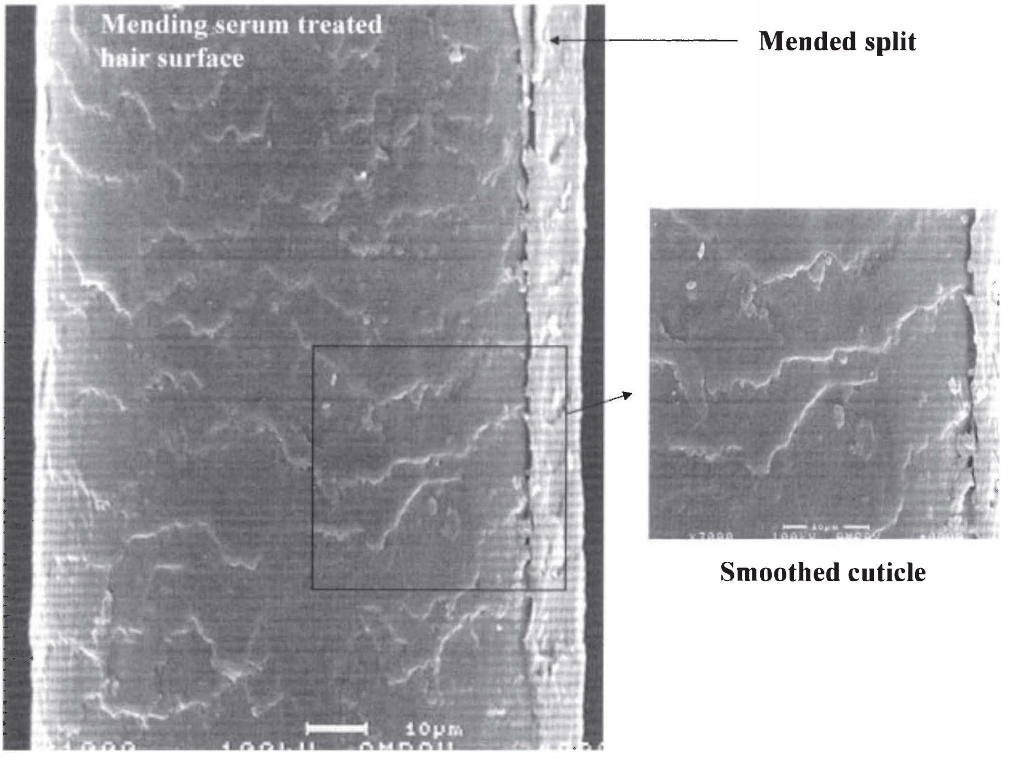


Figure 21. SEM image of hair fiber after mending, showing mended split and smoothed cuticle.

combinations of polymers that form microgel structures after complexation that could also have a positive benefit in the area of hair repair.

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