The mechanics of fixatives as explained by polymer composite principles

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Synopsis

Polymer composite principles are shown to explain the mechanism and performance of fixative-treated hair tresses. This concept is illustrated using cassia and experimental cassia hydroxypropyltrimonium chloride derivatives at two charge densities. Correlations are drawn between polymer film and fixative performance properties, and the primary mechanisms behind the performance of each polymer are suggested. The cationic charge density affects the adhesion and cohesion of these polymers, and the contributions of these two properties to performance are shown.

It is also shown that the relationship between cationic charge density and fixative stiffness of these polymers is dependent on the relative humidity (RH) of the test. The lower charge density polymer yields higher tress stiffness than the higher charge density polymer at 50% RH, but this trend is reversed at 90% RH. A hypothesis is offered in explanation of this phenomenon, relating adhesion and cohesion to the performance of fixative-hair composites. At high humidity, moisture can plasticize the polymers, reducing the cohesive strength, so electrostatic attraction and thus adhesion becomes the dominant force. Evidence to support this hypothesis is given.

INTRODUCTION

Hair fixative gels are widely used to create and maintain a variety of hairstyles. Two important properties desired in hair gel products are stiffness and hold, which are controlled by the fixative polymer in the formulation. To satisfy increasing consumer demands, performance with respect to these properties must be improved relative to the current fixative polymers. Understanding the science behind fixative gel-treated hair is essential to achieving these improvements.

A hair fixative gel is a cosmetic product; however, its performance is governed by polymer composite mechanisms. When a gel is applied to the hair, a polymer-fiber composite is created that is morphologically similar to high performance fiber composites (1) used in load-bearing applications. The differences between fixative-treated hair and industrial fiber composites are primarily in the mode of fabrication and the performance specifications.

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Industrial composites start with the polymer and add fibers for reinforcement; there is a critical amount of fibers that must be achieved for strengthening. In contrast, fixative composites start with fibers (hair), and a minimum amount of polymer gel must be used to achieve composite strength properties. As is the case for the industrial composites, the hair fibers provide the primary strength to the fixative composite. (With respect to fixative gel products, this sometimes goes against popular belief.) In both cases, it is important that the polymer adheres to the fibers (2). The fixative gel glues multiple hair fibers together, creating a composite fiber with a larger effective diameter, and thus, higher stiffness. Good adhesion between the polymer and the fibers allows stress transfer between the polymer and fiber and is necessary to achieve composite properties. Polymer cohesion, which is affected by molecular weight, architecture, crystallinity, polar interactions, hydrogen bonding, environmental conditions and additives, contributes to the composite strength when there is sufficient polymer-hair adhesion (3).

To demonstrate the connection of composite science and cosmetic formulation, the effect of cationic substitution on the polymer film and the composite mechanical properties will be shown for cassia and two experimental hydroxypropyltrimonium chloride derivatives (Lubrizol Advanced Materials, Inc., Noveon® Consumer Specialties). Film testing will show how the cationic charge density affects the cohesive properties of the polymer, and testing fixative-hair composites will provide a measure of the combined adhesive and cohesive properties. The results will be considered with respect to polymer composite principles, and the implications for the balance of adhesion and cohesion in fixative mechanisms will be discussed.

EXPERIMENTAL

MATERIALS

Cassia gum (cassia tora and cassia obtusifolia) and experimental cassia hydroxypropyltrimonium chloride (cassia HPTC) polymers, with cationic substitution levels of 1.8 and 3.0 meq/g, were used for this work. The average repeat units of cassia and cassia HPTC with a charge density of 3.0 meq/g are shown in Figures 1 and 2, respectively. Preparation of these derivatives has been described elsewhere (4). Polymer dispersions were prepared using 0.5, 1.0 and 2.0 weight percent (solids) cassia polymer. The cassia HPTC polymers were cold-water dispersed, and cassia gum was heated to 80°C for 30 minutes to disperse.

SAMPLE PREPARATION AND METHODS

Polymer films were prepared by pouring the dispersions into Teflon-coated foil troughs and allowed to evaporate for a minimum of seven days at 23°C, 50% relative humidity (RH). The resultant dry film was approximately 0.20 mm thick.

Tensile testing of the films was done with a TA.XT.Plus® Texture Analyser (Texture Technologies). All testing was performed at 23°C, 50% RH using the sample geometry described in ASTM D 882-02 (5) and a rate of 5 cm/min. Tensile strength, calculated as the maximum of the stress versus strain curve, and elongation at break were obtained for comparison.
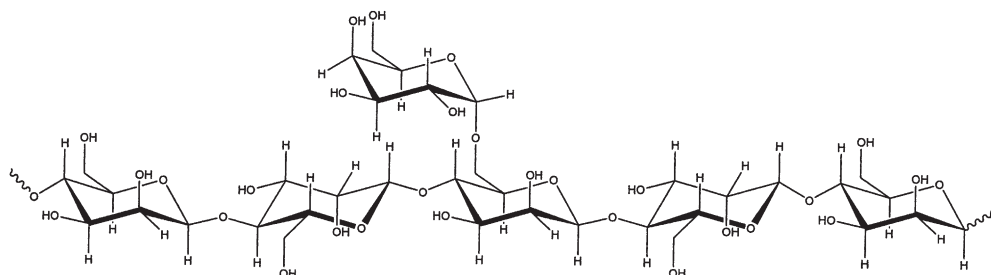
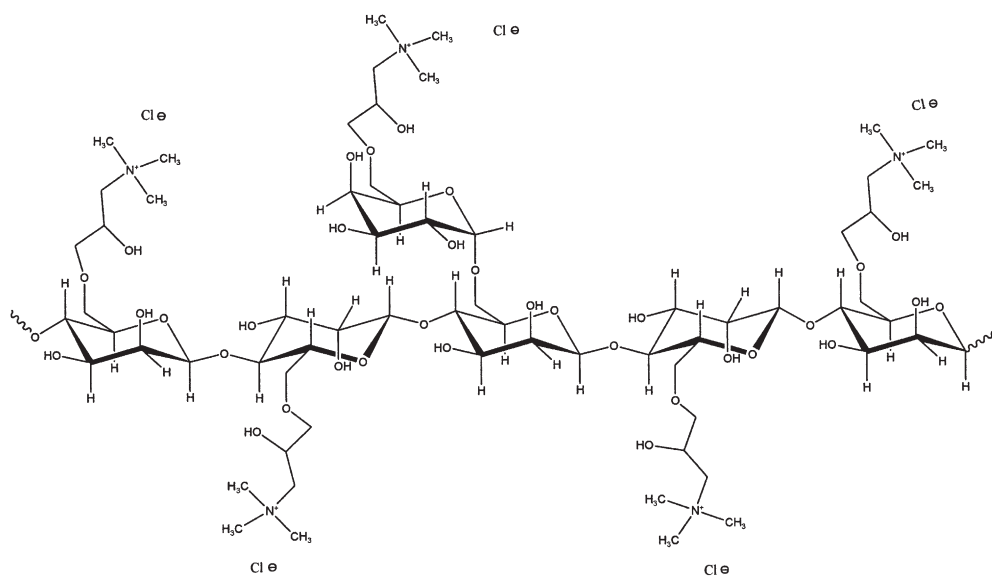**Figure 1.** Average repeat unit for cassia.

Figure 2. Average repeat unit for cassia hydroxypropyltrimonium chloride at a substitution level of 3.0 meq/g.

Dynamic mechanical analysis (DMA) was performed on a TA RSA3 Dynamic Mechanical Analyzer (TA Instruments) using rectangular samples of polymer film. Strain sweeps were first done in tension to determine the linear range of the polymers. Temperature sweeps were then done in tension from –50 to 250°C at a frequency of 1 Hz and a strain of 0.001% in a nitrogen-purged atmosphere. The glass transition temperature (T_g) was chosen as the onset of the decrease in the elastic modulus (E′). Frequency sweeps were done in extension at 23°C and 50% or 90% RH.

The stiffness of the fixative-hair composite samples was performed using a TA.XT.Plus® Texture Analyser in a three-point bend configuration. Composite samples for this test were prepared by applying 0.8 g of polymer dispersion to virgin Chinese hair tresses, which were 2.5 g in weight and 16.5 cm in length. The prepared tresses were sandwiched between perforated, Teflon-coated plates and clamped using spacers to maintain a flat, rectangular geometry while the samples were dried for 24 hours at 23°C, 50% RH. For high humidity testing, the dried samples were conditioned for an additional 24 hours at

25°C, 90% RH. Testing was done using a support span of 2.54 cm and a flexure rate of 40 mm/s. The data were plotted as force versus time. Peak force was used as a measure of stiffness instead of Young's modulus, (6) which is in the linear deformation region of the curve, because it is a better probe of adhesion. (7) Five samples were prepared per polymer, and the averages are reported.

RESULTS

Traditionally, rigid polymers have been used in fixative applications to create stiff-hold hairstyles. It is generally believed that the fixative polymer stiffens the hair since the stiffness of treated hair is more rigid than the untreated hair fibers. However, it will be demonstrated that fixative-treated hair is a polymer-fiber composite. Thus, the hair fibers are the primary source of strength of the composite, and adhesion is of prime importance in achieving polymer composite properties. This does not mean that the cohesive properties are unimportant, as the results for the chosen example will demonstrate. With adequate adhesion, the cohesive strength of the polymer affects the stiffness of the composite. Therefore, the cohesive properties of potential fixative polymers must also be considered. Cohesion of fixative polymers is probed by mechanical tests on thin films.

FILM PROPERTIES

Dynamic mechanical analysis (DMA) and tensile testing were conducted to give complimentary information on polymer cohesion. Tensile data for cassia and two cationic derivatives are shown in Figure 3, plotted as percent elongation to break and tensile strength versus charge density. These results show that as the cationic charge substitution increases, the tensile strength decreases, and the elongation increases. In other words, the quaternary substitution in this example appears to plasticize and thus increase the stress relaxation properties of the polymer. With respect to the chemical structure of cassia, intermolecular hydrogen bonding is expected to drive close packing of the polymer chains and act as a primary contributor to the cohesive strength. The cationic substitution in this example adds flexible short chain branches to the polymer backbone, which cause steric hindrance to close packing, creating additional free volume that gives a plasticization effect to the polymer. Thus, a decrease in the glass transition temperature (T_g) is expected.

DMA was used to measure the T_g, an important parameter for describing amorphous polymer rigidity. The T_g is related to the activation energy needed to enable long-range, coordinated molecular motion; hence, the T_g is related to the cohesive energy density (8) of the polymer and is affected by inter- and intramolecular forces and molecular architecture (9,10). The effect of the level of cationic substitution on the T_g of cassia is shown for the example polymers in Figure 4. The elastic modulus, E', is plotted versus temperature, and the onset of T_g is indicated by the temperature at which E' begins to decrease.

The DMA data reinforce the concept that cationic charge substitution causes steric hindrance to intermolecular attractive forces and consequently lowers the cohesive energy density. The glass transition temperatures for these cassia polymers decrease with increased charge density.
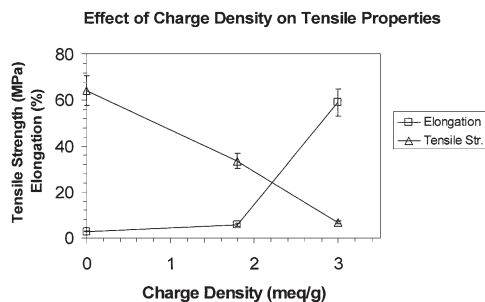
Effect of Charge Density on Tensile Properties

Figure 3. Tensile strength (MPa) and elongation to break (%) versus charge density for films of cassia and cassia hydroxypropyltrimonium chloride polymers. The error bars represent ± one standard deviation.
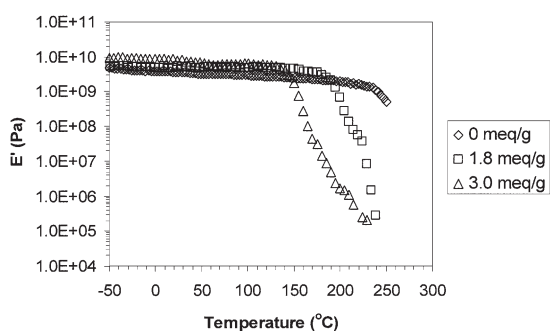

Figure 4. Elastic modulus (E′) versus temperature (°C) for films of cassia and cassia hydroxypropyltrimonium chloride polymers.

POLYMER COMPOSITE PROPERTIES

As stated earlier, the key to achieving composite properties is adhesion between the polymer and fiber. Good adhesion allows stress transfer from the polymer to the fibers, which prevents premature failure of the composite. Furthermore, if the polymer/fiber interface (adhesion) is weak, it will dominate the flexural properties (stiffness) of the composite (11). Consequently, the flexure (three-point bend) test is an indirect measure of fiber/polymer adhesion (12). Considering the composite performance test results along with the polymer film test (cohesion) results allows deductions to be made about the relative contributions of adhesion and cohesion to fixative performance. Since hair has an overall negative charge at neutral pH, cationic substitution enhances the adhesion of cassia to hair through electrostatic bonding, which should facilitate the distinction between the contributions of adhesion and cohesion for this example.

In the three-point bend test, stress is applied to the polymer composite to force failure. The mode(s) of failure depends on the relative strengths of adhesion (polymer to hair) and cohesion (polymer to polymer). If the adhesion to the hair is adequate relative to the applied stress, the cohesive properties of the fixative polymer will contribute to the composite properties. Polymer cohesive properties determine how a polymer responds to applied stress and are influenced by molecular weight (entanglements), architecture (branching, tacticity, etc), crosslinking, crystallinity, attractive forces (hydrogen bonding, van der Waals forces, etc) and plasticization. When stress is applied to a polymer, the way it is

dissipated depends on the cohesive properties of the polymer; it may crack, yield, or craze at failure (13). For example, a stiff, brittle polymer may quickly crack to relieve an applied stress, but plasticization may allow it to relax out the stress and prevent or delay breakage. Even with good adhesion, a polymer composite with poor polymer cohesion results in early failure and ultimately less stiffness. Composite stiffness test results represent the balance of adhesive and cohesive forces under given test conditions.

The average peak force stiffness (at 50% RH) for 0.5, 1.0 and 2.0% (w/w) solutions of the cassia HPTC polymers are shown in Figure 5. Overall, these data show a trend of increasing stiffness with increasing polymer concentration, which is known for fixative polymers. The data also show a trend of higher stiffness for low cationic charge density (CD) polymer relative to the high CD polymer. The effects of concentration and cationic substitution level for this example represent the contribution of polymer cohesive strength to composite stiffness. A higher concentration yields a thicker polymer film, which is stiffer than a thinner film of the same material, and for a given charge density, composite stiffness trends with the cohesive strengths observed in film testing.

The average stiffness data for 2% dispersions, tested at 50% and 90% RH, are shown graphically in Figure 6. Comparison of the stiffness value for cassia with the values for the cationic derivatives highlights the importance of adhesion to composite stiffness. Cassia gum was previously shown to have higher cohesive strength than the cassia HPTC polymers,
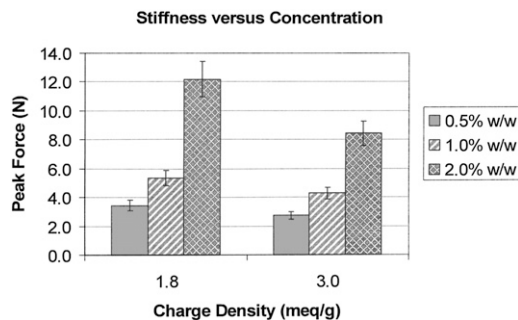

Figure 5. Composite stiffness (peak force) versus concentration for cassia hydroxypropyltrimonium chloride polymers at 50% RH. The error bars represent ± one standard deviation.
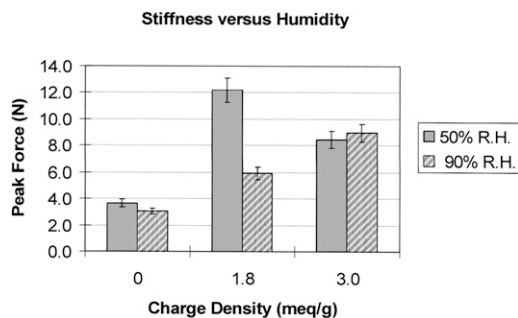

Figure 6. Composite stiffness (peak force) versus charge density at 2% concentration for cassia and cassia hydroxypropyltrimonium chloride polymers at 50% and 90% RH. The error bars represent ± one standard deviation.

yet it has the lowest composite stiffness. It is surmised that adhesive failure is the cause of this difference in composite stiffness between cassia gum and the cassia HPTC derivatives. On the other hand, comparison of the composite stiffness values at 50% RH for the cassia HPTC polymers shows the importance of polymer cohesion. The 3.0 meq/g CD polymer has greater adhesion to hair, but its cohesive properties are lower than the 1.8 meq/g CD polymer. It is deduced that the adhesion of the 1.8 meq/g cationic polymer to the hair is sufficient to withstand the applied flexure stress, so the cohesion of the polymer has a significant influence on composite stiffness. The composite stiffness of the higher CD polymer is relatively insensitive to humidity in comparison to the lower CD polymer, which loses considerable composite stiffness at 90% RH. As a result, the trend in composite stiffness at 50% RH reverses at 90% RH. Composite stiffness for the 3.0 meq/g cationic polymer is greater than that for the 1.8 meq/g polymer at 90% RH. The observed relationship among charge density, stiffness and humidity indicates the relative contributions of adhesion and cohesion for these polymers.

The cationic charge density of cassia HPTC affects the cohesive properties as well as the adhesive properties. The cohesive strength of the polymer decreases with increased charge density, but due to the electrostatic forces between the quaternary groups on the polymer and the negative charges on the hair, the adhesive strength should increase with increased cationic CD. The change in cohesion with charge density has been attributed to steric hindrance of the quaternary groups, which interferes with the intermolecular hydrogen bonding of the polymer chains and causes an increase in free volume or plasticization effect of the polymer. At high humidity, water vapor is absorbed, which affects the polymer properties. If the modulus of the polymer were the only contributing factor to composite stiffness, the stiffness of the lower CD polymer would be expected to drop no lower than the stiffness of the higher CD polymer at 90% RH. This is where the importance of adhesion between the polymer and the hair is apparent. At high humidity, the polymer with higher CD has higher composite stiffness than the polymer with lower charge density. Both the higher and lower CD polymers absorb moisture, which may cause the cohesive properties of the polymers to become more similar at high humidity. Thus, the differences in adhesion between the polymers become discernible, as illustrated at 90% RH, where the composite stiffness of the higher CD polymer is higher than the composite stiffness of the lower CD polymer.

A custom DMA fixture has been designed and fabricated to test the above hypothesis. This apparatus allows DMA frequency sweeps to be run at various, controlled relative humidities. The results for cationic cassia at 50% and 90% RH, plotted as tan delta versus frequency, are shown in Figures 7 and 8, respectively. Tan delta is defined as the ratio
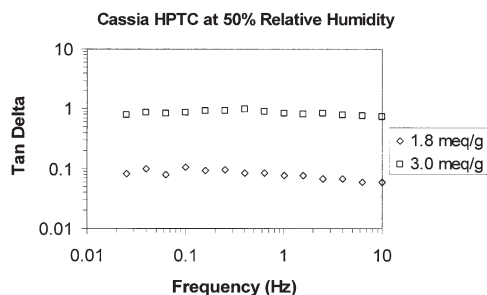

Figure 7. Tan delta versus frequency at 50% relative humidity for cassia hydroxypropyltrimonium chloride polymers.
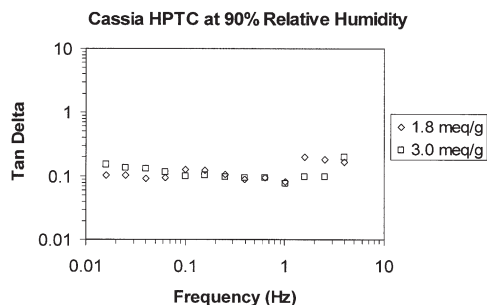
Figure 8. Tan delta versus frequency at 90% relative humidity for cassia hydroxypropyltrimonium chloride polymers.

of the loss modulus (E″) to the storage modulus (E′), and it is a measure of the bulk compliance of the polymer. Higher tan delta values correspond to softer or more compliant polymers, and conversely, lower tan delta values correspond to stiffer polymers. Tan delta at 50% RH confirms the tensile data presented earlier; the lower cationic CD polymer has higher cohesion than the higher CD polymer. Tan delta at 90% RH confirms that the cohesive properties of the cassia HPTC polymers become similar at 90% RH. Thus, the differences observed in composite stiffness at 90% RH are due to the differences in adhesion.

CONCLUSIONS

The application of polymer composite science to fixative-treated hair tresses provides better understanding by giving insight into the mechanisms that govern performance. The relative contributions of adhesion and cohesion to composite stiffness were demonstrated using cassia and cassia hydroxypropyltrimonium chloride polymers as an example. The importance of adhesion was demonstrated by the low composite stiffness values for cassia relative to its HPTC derivatives. The relative contributions of adhesion and cohesion were shown to depend on environmental conditions for the cationic derivatives in the chosen example. Cohesion was dominant at 50% RH, while adhesion became prominent at 90% RH.

ACKNOWLEDGMENTS

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