Bimodal Polymers for Next Generation Hair Styling Products

Keywords: Hair styling polymer, quick setting, humidity resistance

Abstract

The unique bimodal technology was initially designed to enhance hair styling products by improving hold performance in quick setting formulations but has also shown excellent performance properties in most hair styling formulations.

The ability of SYNTRAN® bimodal polymers to balance simultaneously opposing properties can help formulators to produce hair fixative products designed to provide the effectiveness and aesthetic properties demanded by the market.

Recently, two novel bimodal polymers, SYNTRAN® PC 5100 and SYNTRAN® PC 5112, have become available. SYNTRAN® EX107 is available as a prototype for formulators who wish to develop a unique product that has higher tolerance to ethanol.

Bimodal polymers exhibit good performance when evaluated on blow-dried hair by providing high-humidity curl retention that is superior to formulations containing PVP-type fixatives. They also show quick setting properties, which make them as alternatives to current hair care polymers and viable components for the next generation of styling aid products.

Introduction

Hair fixative products are available to consumers in a variety of forms such as aerosol, pump spray, gel, mousse, and styling lotion. Regardless of these differences, the ultimate goal is the same: the uniform application of a clear polymeric material to the hair to achieve certain improvements in appearance and manageability.

Hair styling and fixative products help build the interactive forces between hair fibers, by promoting adherence to the adjacent hairs so they can keep a particular shape or configuration as the polymer dries.

Consumers expect a number of often-contradictory properties from hair fixative products. The hairstyle must be held firmly in place under all conditions of humidity, but the hair must not feel too stiff. The spray must dry quickly after application, but the resin solution must be able to flow along the hair shaft to fiber/fiber junctions. The hair must appear natural and glossy and be easily combed, both when wet and when dry. The dried resin must not crack or produce flakes when combed or brushed, and must not make the hair feel tacky or sticky, even under conditions of high humidity. Finally, the fixative polymer must be readily removable from the hair by shampooing.

Commonly used fixative polymers are PVP (Polyvinylpyrrolidone) and PVP/VA-Copolymers (Polyvinylpyrrolidone/Vinyl Acetate). The fixative properties can be varied over a wide range by using PVP's with different molecular weight, e.g., PVP K 30 or PVP K 90. Co-polymerizing PVP with vinyl acetate (VA) provides a less tacky film that is more resistant to humidity than the PVP. Furthermore, Polyquaternium–46, a cationic polymer often used if there is a need for setting as well as conditioning properties, can provide improved hold in addition to more manageable hair. Cationic polymers have been used as a single polymer or in combination with PVP/VA copolymers.

Acrylic Copolymers are an alternative to these traditional polymers. Interpolymer recently developed an innovative technology identified as »bimodal«. This refers to its structure which is composed of two different types of acrylic polymer molecules: one with anionic and the other...
one with cationic functionalities (Patent pending). These bimodal polymers have good affinity for keratin surfaces and show clear advantages in hair fixative formulations.

**Bimodal Polymers: Structural Properties**

Interpolymer’s unique bimodal technology is designed to enhance hair styling products by improving «hold performance». These properties are accomplished through an innovative technology that uses a bimodal, interpenetrating network delivering both cationic and anionic functions. The result is a reversible, cross-linked polymer complex achieved by the ionic associations of the two types of polymer chains which provides both holding power and ease of removal. The anionic chain contributes to the polymer’s removal properties and the cationic chain imparts strong hold and ease of styling. The bimodal polymers have film formation temperatures that are balanced to give a pleasant crisp feel without flaking and because of their ionic crosslinking, impart improved flexibility and humidity resistance.

Fig. 1 shows the charge density around one chain of an acrylic copolymer. It demonstrates the strong ionic association that can be formed when two or more chains associate to form an interpenetrating network. The amino function is placed in an exposed position to interact with the acidic part of the anionic acrylic copolymer chain to form the interpenetrating network (Fig. 2). Co-monomer selection and molecular weight control allow Interpolymer to optimize the steric hindrances and ionic interactions which result in specific setting and hold properties. Polymer composition plays an important role in this geometrical and electrical interaction. The inclusion of strongly electropositive or electronegative groups on separate molecules causes an inductive shift of electrons. This shift plays an important role in the polymer’s cohesive and adhesive properties. Since the bimodal polymers are composed of both electropositive and electronegative groups, there is a great potential for the polymer chains to exhibit this shift in electron density. At large distances, these polymer chains would behave like an electrically neutral system. However, as the ionic groups are brought into close proximity to their counter-ion during the drying process, strong secondary bond forces begin to exert their influence and give the bimodal polymers their unique characteristics. Fig. 3 illustrates the ionic interaction during the drying process.

This novel technology relies on the ability to produce stable dispersion and solutions containing polymer molecules with different ionic changes. During the drying process, the bimodal polymer will form an ionic complex, as described above, even before the final film is completely dry and sets on the hair. The resultant complex or «gel» prevents the formulation from migrating even before the water or solvent has completely evaporated. The ability of bimodal polymers to set quickly under high humidity conditions make them a reliable alternative to current hair care polymers. There are significant structural differences between SYNTRAN PC 5100 and SYNTRAN PC 5112 which allow the formulator to select the desired aesthetic properties required for a particular formulation. Typically the SYNTRAN PC 5112 is used in applications where a softer more natural feel is desired.
Application Evaluation of Bimodal Polymers

Bimodal polymers can be formulated in any ionic system, in aqueous or hydro/alcohol dispersions and emulsions, however their uses in aerosol sprays have not yet been studied. Promising results have been obtained in ultra-hold fixing pump sprays as well as styling foams, lotions or gels. The bimodal polymers are compatible to varying degrees with many rheology modifiers, including carboxylated thickeners, cellulose derivatives, and other synthetic thickeners, but formulations should be carefully evaluated to ensure full compatibility.

### Ingredients Weight %

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<th>Ingredients</th>
<th>Weight %</th>
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<td>DMDMH</td>
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<td>Oleth-20</td>
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<td>Panthenol</td>
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<tr>
<td>Glycerin USP 99.7%</td>
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<tr>
<td>Sodium EDTA</td>
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<tr>
<td>Fragrance #98444</td>
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<tr>
<td><strong>Total</strong></td>
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Table 1 Texturizing Gel Formula @ 3% N.V.

### Ingredients Weight %

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<td>CETRIMONIUM CHLORIDE</td>
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<td>Glycerine 99% USP</td>
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<tr>
<td><strong>Total</strong></td>
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</table>

Table 2 Foaming Mousse Formula @ 5% N.V.

### Ingredients Weight %

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<td>Coco Betaine</td>
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<td>CETRIMONIUM CHLORIDE</td>
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<td>Panthenol</td>
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<tr>
<td>Hydrolysed Wheat protein</td>
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<tr>
<td>Fragrance</td>
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<tr>
<td><strong>Total</strong></td>
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</tr>
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</table>

Table 3 Styling Lotion Formula @ 7% N.V.

**Table 4 Test Protocol for Dry Hair Evaluation**

- **Initial Hold (no comb)**
  - Blow dry or allow hair to set in a desired style with natural pattern of hair. Once set, note the extent that the hair accepts the desired style.

- **Naturalness of Hold**
  - Rake fingers or comb through finished hair style. Note crispness and adhesion between fibers to form rigid fiber bundles.

- **Hold (comb x5)**
  - Blow dry or allow hair to set in a style that opposes natural pattern of hair. Once set, comb through the hair five times with fine tooth comb or vent brush in direction of style. Note percentage of style retained.

- **Curl Character**
  - Let hair dry into natural curl pattern or set hair in curl pattern. Note character of curls obtained.

- **Frizz**
  - Note the percentage of frizz from tips to root end of hair.

- **Stiffness**
  - Rake fingers or comb through finished hair style. Note crispness and adhesion between fibers to form rigid fiber bundles.

- **Flaking**
  - Apply styling products as per directions. Let dry, then brush through the hair to determine if flaking is noted on hair.

- **Tactile Smoothness**
  - Starting at root end, compress small section of hair between thumb and index finger and gently pull along length of hair through tip. Do this on all four quadrants.

- **Dry Residual Feel**
  - Blow dry hair. Run fingers through hair and note if hair surface and/or fingers appear to be coated.

- **Dry Combing**
  - Remove tangles from hair. Start at root end, comb swath of hair with medium tooth comb. Note resistance to combing and scraping sound. Do this on minimum of four different sections of test area.

- **Static / Flyaway**
  - Brush a section of hair with a plastic brush three times. Determine amount of ballooning or separation of fibers and note attraction of hair to brush.

- **Shine**
  - When hair is dry, comb and align hair uniformly. With a good light source, make your observation.
Experimental Details

For three control formulations, a texturizing gel (Table 1), a foaming mousse (Table 2), and a styling lotion (Table 3), the dry hair evaluation profiles have been outlined. The test protocol for each parameter tested is summarized in Table 4.

High humidity curl retention was also performed for the three control formulations. Results will show the direct comparison between formulations based on different polymers but containing the same active content: PVP K30, PVP/VA 70:30, Polyquaternium-46, Polyquaternium-4, SYNTRAN PC 5100, SYNTRAN PC 5112 and SYNTRAN EX 107.

High Humidity Curl Retention Test

Hair swatches were cleaned. All hair samples were approximately 6.5 grams in weight and 25 cm in length. The swatches were immediately coated with the appropriate testing solution and combed to distribute the solution evenly on the hair. The cleaned samples were then curled using a curling rod and allowed to dry overnight at room temperature. The swatches were hung vertically and curl retention was measured for the initial reading. The hair swatches are placed in a humidity chamber and measurements (position of bottom of curl) are recorded hourly for the next seven hours. Curl length was determined as a function of time.

Percent Curl Retention is calculated by means of the following equation:

\[
\% \text{ Curl Retention} = 100 \times \frac{[L - L_f]}{(L - L_0)}
\]

where

- \(L\) = length of hair fully extended (before curling)
- \(L_0\) = length of curled hair before exposure
- \(L_f\) = length of curled hair after exposure as a function of time

The results are shown in Figs. 4, 5 and 6.

Evaluations of the Three Control Formulations on Dry Hair

Hair swatches similar to those for the humidity curl retention test were treat-
ed in the same manner and evaluated for physical characteristics. The results of these evaluations are found in Figs. 7, 8, and 9, and are arranged on spider charts with the rating system going from 1 to 6 (6 = the best). These evaluations were performed by JJC Creative Consulting, LLC, of Trumbull, CT.

Texturizing Gel
Performance of SYNTRAN bimodal polymers vs PVP K30, PVP/VA 70:30 and polyquaternium-46 in a texturizing gel (for composition see Table 1) was investigated to determine the performance profile on dry hair (Fig. 7). SYNTRAN PC 5100 and SYNTRAN EX107 show clear advantages for almost all parameters tested in the dry evaluation. The gel based on SYNTRAN PC 5100 provides superior dry combing characteristics. The hair can be combed easily from root to tip without resistance and without any hair surface scraping sound. The high humidity curl retention test clearly demonstrates the bimodal polymer’s superior performance compared to the traditional PVP/VA (Fig. 4). The gel formulated with SYNTRAN PC 5100 retained 75% of initial curl after 7 hours under 90% relative humidity at 37°C.

Foaming Mousse
Fig. 8 displays the dry hair evaluation profile of the bimodal polymers, PVP, PVP/VA, polyquaternium-46 and polyquaternium-4 in a foaming mousse at 5% active (for composition see Table 2). SYNTRAN PC 5112 yields stiffness that is superior to the other polymers. SYNTRAN EX107 and PC5100 had comparable stiffness to PVP K30. However, in this formulation, bimodal polymers show very good tactile smoothness and do not provide a hard, stiff feel. It is important to note that dry performance of the bimodal polymers, as with other polymers, is formulation specific. Tactile perceptions can be modified using the bimodal polymers while still retaining their excellent holding properties. High humidity curl retention evaluations were also conducted for the same series of polymers (except the polyquaterniums). All curls were evaluated at 97%
relative humidity and 28°C for a period of 7 hours. Fig. 5 shows that SYNTTRAN PC 5100 and EX107 perform very well and comparably to each other while SYNTTRAN PC 5112 holds 50% curl retention. PVP K30 holds only 22% after 7 hours.

### Conclusion

This novel bimodal polymer technology is based on unique, interpenetrating polymer networks. By incorporating both cationic and anionic functionalities, the bimodal polymers offer a formulator the opportunity to improve performance in a variety of fixative formulas. Bimodal polymers can be formulated in pump sprays, gels, mousses or lotions.

The test data indicate that bimodal polymers provide high humidity curl retention superior to formulations containing PVP-type fixatives. These polymers also exhibit good aesthetic performance when evaluated on dried hair. This versatility makes them a reliable alternative to current hair care polymers and for the next generation of hair styling products.

### Acknowledgements

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