New Hybrid Polymer for Hair Spray Formulations

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ABSTRACT: *Crotonic acid/vinyl C8–12 isoalkyl esters/VA/bis-vinyldimethicone crosspolymer is a new hybrid polymer for use in hair sprays. This highly branched block copolymer is shown to give hair a firm hold yet soft, natural feel. It is recommended for use in quick-drying, low-tack hair sprays with high water content.*

When choosing a hair spray, consumers are often guided by the degree of hold the product offers.[1] However, surveys and market studies show that most respondents consider a pleasant touch to be just as important as good hold.[2]

These contradictory goals present formulators with a challenge:[3] a hair spray that gives a very firm hold has poor tactile properties—the hair feels unnaturally stiff, hard, inflexible and rough. Conversely, if a hair spray is to impart a pleasant, soft and natural feel, the hold will inevitably be reduced.

Other requirements, too, are contradictory.[4,5] For example, the polymer film that forms on the hair must be readily soluble or dispersible in water so it can be washed out with water and shampoo, but it must not be hygroscopic or the hair will become tacky in humid air and lose its hold. Various desirable mechanical properties—failure stress and shear strength; elasticity and hardness—are likewise contradictory, as are the polymer film's cohesive and adhesive properties.

For environmental reasons, hair spray manufacturers also seek significant reductions in the content of volatile organic compounds (VOC).[3,6] If this involves substituting water for a considerable proportion of the ethanol, a highly volatile solvent, and if conventional polymer systems are used, both the formulations' technical quality and the useful properties of hair spray products will be degraded. One of the consequences is an increase in the polymer solution's viscosity and surface tension, which leads to the formation of large aerosol particles and prevents uniform distribution of the solution on the hair. In addition, a higher water content in organic polymers typically results in longer drying times and a more tacky film.

Modifying Properties by Copolymerization

Today, the principal styling ingredient in hair sprays is usually a copolymer. Block and comb polymers are still used relatively infrequently. Many polymer properties can be customized by judicious selection of the monomers or—in the case of block and comb polymers—of the polymer segments used. For example, a balance can be achieved between the hydrophilic and hydrophobic properties, as well as between conflicting mechanical properties.[4] Nevertheless, the authors' experience in testing commercially used products indicates that the conflict between hold and feel remains if the polymer contains only purely organic building blocks.

One approach to resolving the feel-vs.-hold conflict uses silicones. Silicones are known for their friction-lowering, and hence feel-enhancing effect.[7] The friction-lowering effect is a result of the flexible molecular skeleton that characterizes the silicones. The polysiloxane chains are highly mobile and thus enable silicone-treated hair or textile fibers to slip past each other very easily; friction between the treated fibers and other materials is likewise reduced. Silicone products improve the feel of hair and its combability. Furthermore, silicones have a low surface tension as well as a hydrophobic effect. The low surface tension increases the wetting and spreading behavior. The hydrophobicity helps to maintain the hold properties even at high humidity. Therefore, hybrid polymers combining organic and silicone building blocks in a copolymer should, in theory, be able to reconcile the contradictory requirements of good hold and natural feel.

A New Hair Styling Product

Wacker Silicones product developers created and screened several different hybrid polymers made up of organic and silicone segments or "blocks." The starting point for selecting the organic building blocks was a group of monomers that had already proven successful in conventional hair styling polymers. The silicone blocks were selected from divinylpolydimethylsiloxanes. The hybrid polymers were tested principally for styling performance and ease of handling. Among the polymers tested, crotonic acid/vinyl C8–12 isoalkyl esters/VA/bis-vinyldimethicone crosspolymer proved the most suitable for use as a hair styling polymer. For convenience in this article, this new polymer[a] will be referred to as the silicone/vinyl acetate copolymer or SVAC.

[a] *Wacker-Belsil P101 (INCI: Crotonic Acid/Vinyl C8–12 Isoalkyl Esters/VA/Bis-Vinyldimethicone Crosspolymer) is a product of Wacker Chemie AG. Wacker-Belsil is a registered trademark of Wacker Chemie AG.*

Structure: The structure of this highly branched block copolymer is illustrated schematically in **Figure 1**. The macromolecules consist of two different building blocks: an organic polymer segment and a silicone block. Branching is effected by the silicone blocks. The chain lengths of the two blocks and the molecular weight of SVAC have been optimized.

The organic block is mostly vinyl acetate with a sprinkling of crotonic acid and vinyl C8–12 isoalkyl ester. The silicone block consists of polydimethylsiloxane. The silicone blocks have reactive terminal groups to which the organic polymer segments bond during production.

The organic polymer segments impart the required hold. They not only provide the necessary adhesion to the surface of the hair fibers, but also make it possible to wash out the polymer. The silicone blocks improve the feel (see **Bereck Model**) and prevent the polymer film from becoming tacky due to water absorption. Thus, they enhance the hydrophobic property already conferred on the polymer by the polyvinyl acetate chains. Furthermore, they keep the polymer's surface tension low.

Physical properties: SVAC is a practically colorless, nonhygroscopic solid that dissolves completely in ethanol or in ethanol/water mixtures, but also disperses in water. Even after a freeze/thaw cycle in which an aqueous ethanolic solution of polymer was cooled to –20°C, the polymer remained fully dissolved. This is important for applications in spray cans because the temperature in the spray head is apt to drop abruptly during spraying. If the polymer were to precipitate out, it could block the valve. In this case, however, there is no risk that SVAC will block the valve.

Electron micrographs of cast samples and sprayed films (**Figure 2**) show that the silicone blocks in the SVAC are arranged in small domains. Material with a higher atomic number has a higher scattering cross section and therefore leads to stronger scattering. For this reason, the silicone domains appear black. With the help of energy dispersive X-ray spectroscopy (EDX), it is possible to show that the black areas—i.e. the

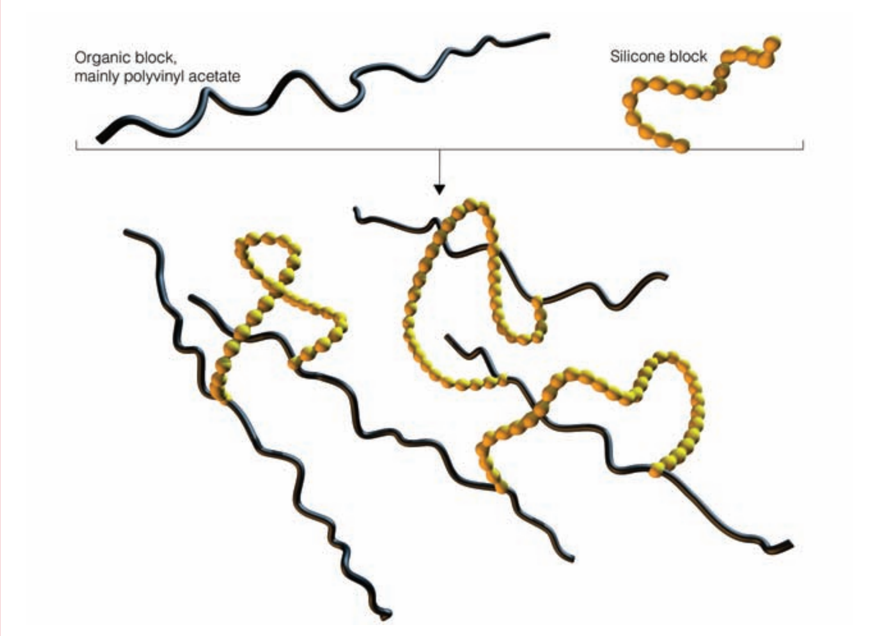

Figure 1. Schematic structural model of crotonic acid/vinyl C8–12 isoalkyl esters/VA/bis-vinyldimethicone crosspolymer

BERECK MODEL

To understand the silicone/vinyl acetate copolymer, or SVAC, discussed in this article, and in particular to understand how it works, consider the Bereck model originally used in textile engineering to describe the interaction between an aminofunctional silicone and a cotton fiber.[10] In this model, the silicone is anchored via its amino groups to the fiber such that the unsubstituted polydimethylsiloxane chain segments between the amino groups are in the form of loops directed away from the fiber surface. These flexible and hydrophobic loops, which are typical of silicones, have a lubricating effect. They are responsible for the pleasant tactile properties, such as soft feel, of silicone-treated textiles.

This model helps to illustrate how the SVAC works. The macromolecules are anchored to the surface of the hair fibers via the crotonic acid in the organic blocks. The polymer chain between two points of anchorage resembles a loop. It consists predominantly of polydimethylsiloxane, which forms the long, central part of the loop. The surface of the hair fiber is thus covered with movable silicone loops (**Figure 7**), and these strongly reduce interfiber friction, friction between fiber and skin and friction between fiber and comb. The hair accordingly feels pleasantly silky and soft, and is easy to comb.

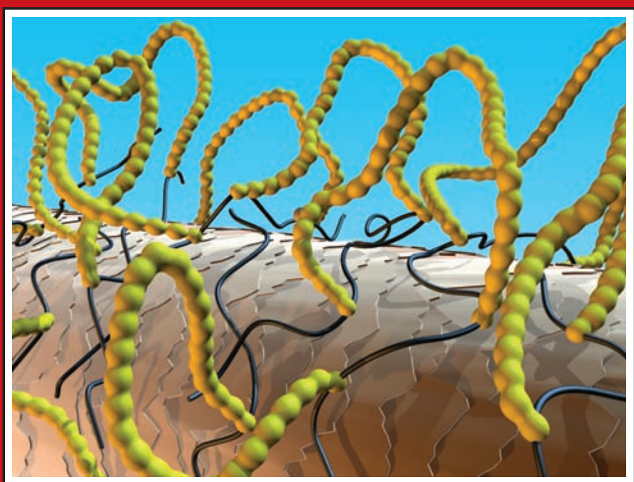

Figure 7. Silicone loops reduce interfiber friction between hair fibers, explaining the soft feel of hair styled with the organic-silicone hybrid polymer.

domains—consist mainly of silicon atoms. However, because these domains are mostly smaller than 50 nanometers (nm), SVAC films are transparent.

The glass transition temperature was determined by differential scanning calorimetry (DSC). It is slightly below 40°C and thus a good 10°C lower than the glass transition temperature of comparable silicone-free copolymers. The low glass transition temperature shows SVAC to be a relatively soft, flexible material with no tendency to form polymer flakes on the hair.

Technical properties: SVAC's technical properties were investigated using test formulations that differed in their polymer and water contents. The formulations were limited to the essential components, as shown in **Formula 1** and **Formula 2** for two different, typical polymer contents.

The viscosity of solutions of SVAC, unlike that of most organic polymers, is low even when the proportion of water is high. This was shown in tests performed on formulations that contained no propellant, but did contain 35% w/w water; this corresponds to 20% w/w water in a propellant-containing final formulation. The polymer content was varied between 5% and 15%, equivalent to 3–9% polymer in spray with propellant. These test formulations proved to be only half as viscous as reference formulations in which the hybrid polymer had been replaced by a vinyl acetate-crotonate-neodecanoate copolymer (**Figure 3**). SVAC is miscible with organic polymers. The viscosity of the solution can be adjusted as required by adding an organic polymer.

Because formulations containing SVAC have low viscosity, they can be sprayed as a fine aerosol. Spray[b] from the test formulations (40% w/w dimethyl ether as propellant) contained aerosol particles ranging in size from 52 µm to 85 µm. Particle size was measured with a laser particle size analyzer[c] by means of light diffraction at a wavelength of 632.8 nm.

Aqueous ethanolic formulations based on the new hybrid polymer dry quickly. In panel tests, the participants found hair tresses treated with the **Formula 2** test formulation (6% w/w polymer content) to be tacky for only 23 sec and dry just 40 sec after they had been sprayed. Tresses treated with polymer blends of the hybrid polymer and vinyl acetate-crotonate-neodecanoate copolymer took longer to dry.

To ensure that the hair style returns to its original shape after mechanical loading such as gusts of wind, the sprayed hair must remain elastic. The three-point

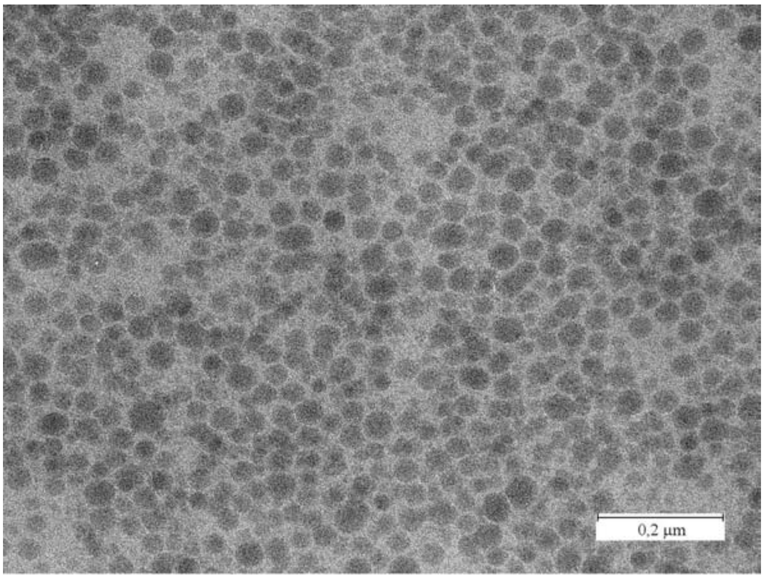

Figure 2. TEM micrograph of a sprayed film of crotonic acid/vinyl C8–12 isoalkyl esters/VA/bis-vinyldimethicone crosspolymer

Formula 1. Hair spray test formulation with 4.5% hybrid polymer

A.	Ethanol	33.33% w/w
	Aminomethylpropanol, 30%	0.68
	Water *(aqua)*	21.50
B.	Crotonic acid/vinyl C8–12 isoalkyl esters/VA/bis-vinyldimethicone crosspolymer (Wacker-Belsil P101, Wacker)	4.50
C.	Dimethyl ether	40.00
		100.00

Procedure: Mix A. Dissolve B into A. Fill the solution into aluminum cans and charge with propellant C. *Physical properties:* Appearance: transparent; pH ~ 7; viscosity: 8.9 cst.

Formula 2. Hair spray test formulation with 6.0% hybrid polymer

A.	Ethanol	32.21% w/w
	Aminomethylpropanol, 30%	0.90
	Water *(aqua)*	20.89
B.	Crotonic acid/vinyl C8–12 isoalkyl esters/VA/bis-vinyldimethicone crosspolymer (Wacker-Belsil P101, Wacker)	4.50
C.	Dimethyl ether	40.00
		100.00

Procedure: Mix A. Dissolve B in A. Fill the solution into aluminum cans and charge with propellant C. *Physical properties:* Appearance: transparent; pH ~ 7; viscosity: 8.9 cst.

[b] *The spray was generated with ST300T spray head and LI valve (with aluminum Microflex mounting cup, Perbunan outer gasket, Butyl U-133 G-1978 inner gasket, 1 x 0.33-mm stem and LI-98 RTP 0.5-mm housing). All equipment was obtained from Lindal, Bad Oldesloe, Germany.*
[c] *Helos laser particle size analyzer, Sympatec GmbH, Clausthal-Zellerfeld, Germany*

bending test[8] showed that hair tresses treated with SVAC retained their elasticity even after repeated mechanical loading. **Figure 4** shows the results for the test formulation with a polymer content of 4.5%. The bending tests were carried out at 65% relative humidity and 23°C.

The new hybrid polymer absorbs only a very small amount of water and is thus only slightly softened by water. The hold imparted by the polymer is therefore retained in humid air. Proof of this was provided by curl retention tests (**Figure 5**) that were carried out at 90% relative humidity and 23°C. The curl retention values measured under these conditions ranged from 85% to 95% depending on the hybrid polymer content. The tests were performed on tresses of brown European hair (3.5–4 g per 15-cm strand of hair). The tresses were wound around a polyvinyl chloride rod of 11 mm diameter and then, when dry, sprayed with the test hair spray formulations.

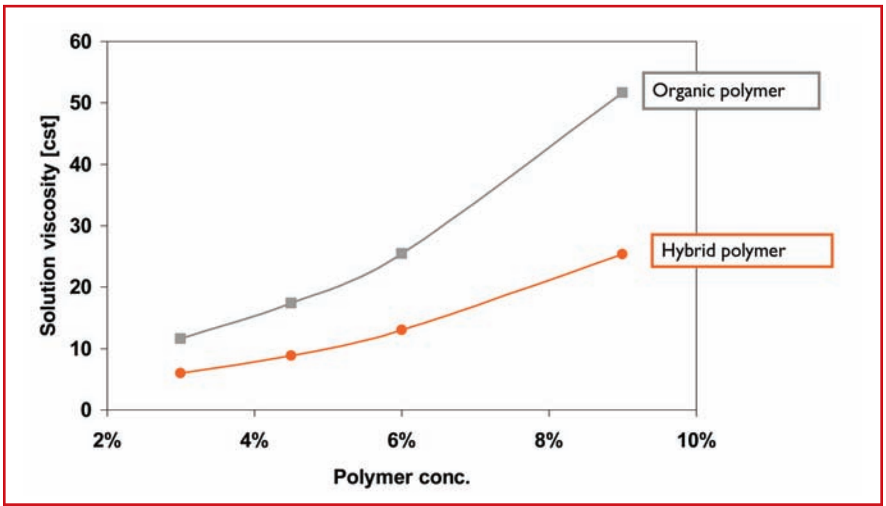

Figure 3. Viscosity of aqueous ethanol formulations of an organic-silicone hybrid polymer and a comparable organic polymer
Organic polymer = vinyl acetate-crotonate-neodecanoate copolymer
Hybrid polymer = crotonic acid/vinyl C8–12 isoalkyl esters/VA/bis-vinyldimethicone crosspolymer

Effectiveness: In panel tests, all the participants rated the SVAC positively and thought it well-balanced. They were asked in a number of trials to compare the effects of SVAC-based test formulations (**Formulas 1** and **2**) with those of commercially available hair sprays (**Figure 6**).

The first comparative product (Benchmark 1) claimed to impart a "firm hold." The testers judged the effect of the test formulations (**Formulas 1** and **2**) as being somewhat more balanced than the comparative product. They found only a small or no difference in hold with **Formula 1** and **Formula 2**, respectively, but confirmed that the SVAC-treated hair tresses had

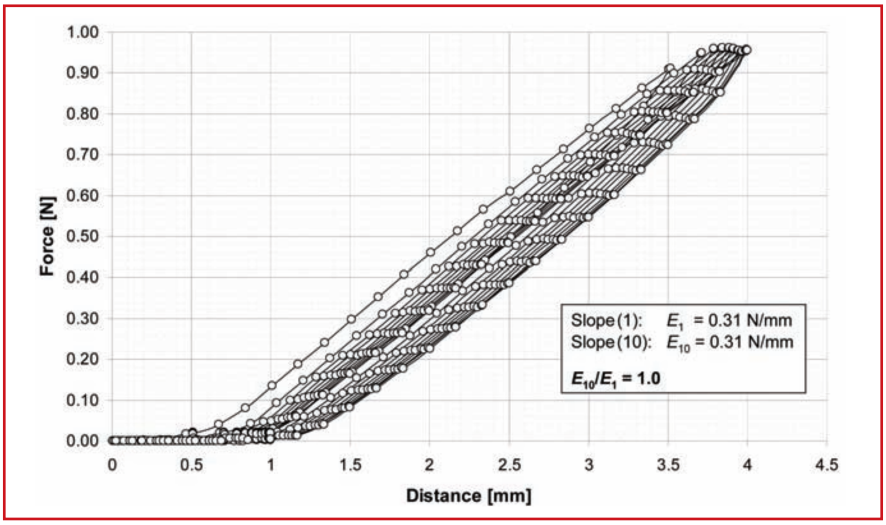

Figure 4. Results of the three-point bending test (10 cycles, 65% RH, 23°C) using hair tresses treated with the Formula 1

more pleasant tactile properties, such as softness, smoothness and flexibility before and after combing.

For the second benchmark test, a product was used that promised a high level of flexibility. This time, the testers considered the SVAC-containing formulations to be superior with respect to softness, hold and combability.

In the third comparative test (Benchmark 3), the effects of the test formulations were compared with those of a hair spray that marketed an "extra-strong hold." Here, the panel participants rated the test formulations as imparting clearly superior softness and flexibility to the hair. The test formulation containing 6% w/w SVAC was considered to impart a slightly better hold than the comparative product.

Summary and Outlook

The test results show that crotonic acid/vinyl C8–12 isoalkyl esters/VA/bis-vinyldimethicone crosspolymer, called SVAC in this article, combines the useful properties of organic polymers with those of silicones. Because this new hybrid polymer is not hygroscopic, even formulations with a high proportion of water do not produce a tacky film. Thus, SVAC allows hair sprays to be formulated with a high proportion of water.

Formulated in a hair spray, SVAC was tested in accordance with the Organization for Economic Cooperation and Development (OECD) guideline[9] for its aerosol inhalation toxicity. No relevant effects were produced in this test, which means the product is classified as "non-dangerous" according to hazardous substances legislation.

Used as a hair styling polymer, SVAC can combine the hitherto conflicting properties of good hold and natural feel. The hybrid polymer thus paves the way toward a new generation of hair sprays. Hair treated with a spray based on SVAC dries quickly, feels silky-soft and pleasant, holds well, retains its shape even in humid air, does not become tacky and is easy to comb. SVAC is also suitable for pump spray formulations. Its use in mousse is currently under test. Initial results are promising. Additional tests are currently underway on variants that impart a firmer hold.

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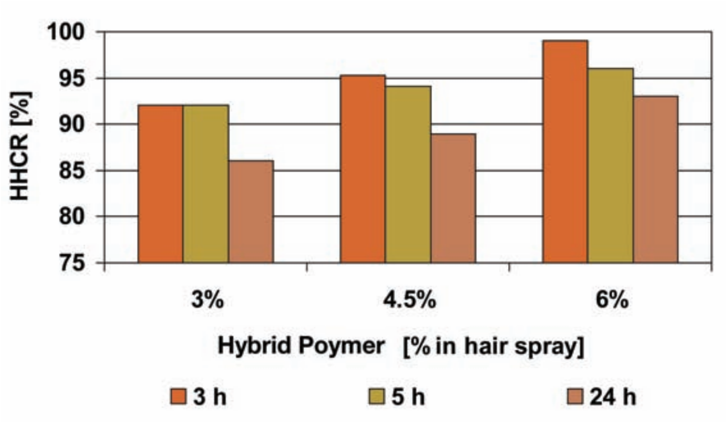

Figure 5. High humidity curl retention (HHCR) (90% RH, 23°C) of the organic-silicone hybrid polymer crotonic acid/vinyl C8–12 isoalkyl esters/VA/bis-vinyldimethicone crosspolymer

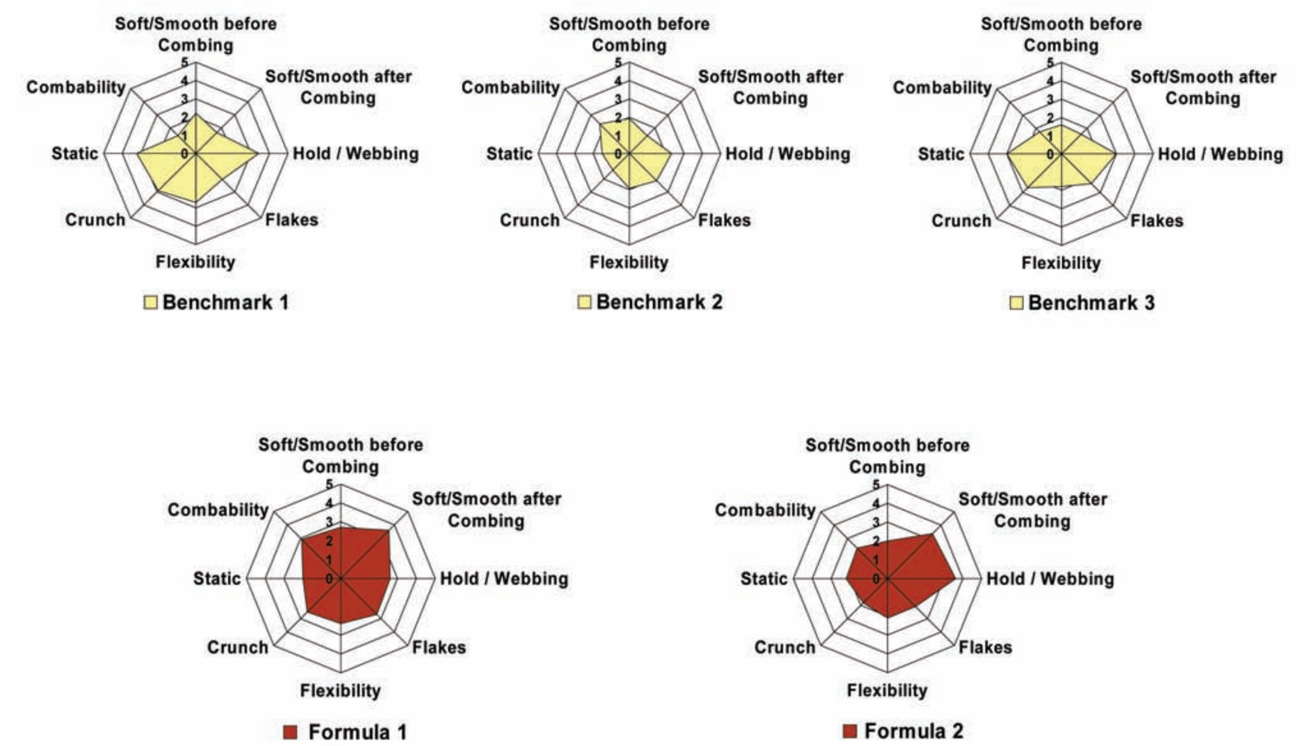

Figure 6. Specific properties of hair tresses treated with Formula 1 (organic-silicone hybrid polymer at 4.5% w/w) and Formula 2 (organic-silicone hybrid polymer at 6% w/w) compared with commercially available hair spray products that claim to offer "strong hold" (Benchmark 1), "flexibility" (Benchmark 2) or "extra-strong hold" (Benchmark 3). Each graphic represents poor performance at the center and improving performance at increasing distances from the center.