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A photograph of a woman with purple hair and a man with a beard in a barbershop setting. The woman is leaning over the man, who is sitting in a barber chair. The background shows a barbershop with various tools and equipment.

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THE FINAL CUT
TOP HAIR STYLISTS DISH
ON WHAT'S IN & WHAT'S OUT

**SHAPE &
RESHAPE**
A MULTI-BENEFIT HAIR SPRAY
POLYMER FOR STYLES THAT
MOVE FROM DAY TO NIGHT

Shape & Re-Shape

A multi-benefit hair spray polymer for styles that move from day to night

Linda C. Foltis, David C Streuli, Silke Langer and Penny Antonopoulos • Ashland Inc.

HAIR IS OUR MOST VALUABLE ACCESSORY; it reflects health and beauty with individual social and cultural significance. From a psychological view, it can define our day. The evolving beauty consumer is no longer defined by gender, ethnicity or age. In hair care, consumers seek products that perform, meet their values, and deliver a “good hair” day, every day! On the scientific side, hair is a complex biopolymer with behavioral responses to the environment, chemical treatments and heat styling. With advances in styling capabilities, in both products and tools, it is important to understand how ingredients, product applications, and styling tools interact with the hair fiber assembly to optimize the desired performance.

Hair spray, invented in 1948 as a consumer outlet for aerosol production after WW II, today represents the largest share of the styling category with the US holding the dominant share in the global market. The aerosol hair spray industry has weathered several regulatory hurdles and continues to reinvent itself to stay current with today’s hair styling trends. Specifically designed for the hair spray formulations of the 1970s where hair was set, sprayed daily, and cleansed with a bi-weekly or weekly shampoo; the monoalkyl esters of PVM/MA copolymer (Gantrez esters) delivered effective non-dulling hold, no buildup, restyle/brush through and good shampoo removability. As we fast-forward to today—the hair styling market is driven by key trends of personalization with style-versatility, selfie-ready with the rise of the digital era, preservation of style & color and ‘less is more’. PVM/MA ester polymers provide long term hold plus benefits of shine, thermal styling, moveability and brushability to meet the dynamic demands of professional stylists and consumers’ styling needs.

Monalkyl Esters of PVM/MA Copolymer

The architecture of the chemistry provides the structure-property relationship tied to the benefits observed in hair spray formulations.

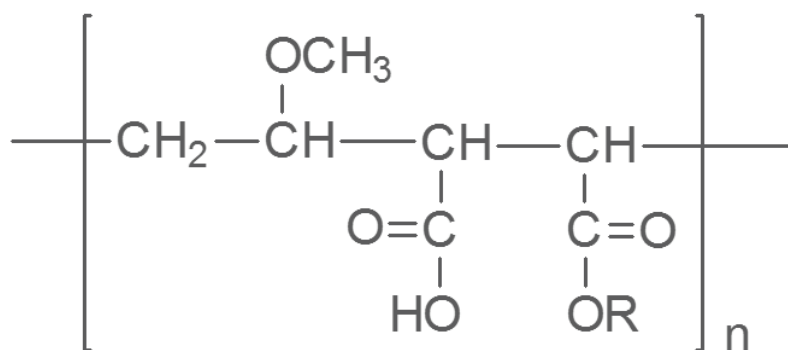
The back-bone is an alternating copolymer of methyl vinyl ether and maleic anhydride. This back-bone is bioadhesive and oxygen-permeating – with traditional uses in used in wound care and oral care. The methyl vinyl ether contributes to the flexibility of the film while the maleic anhydride provides the bonding



Meeting today’s artistic styles across age, gender and hair types.

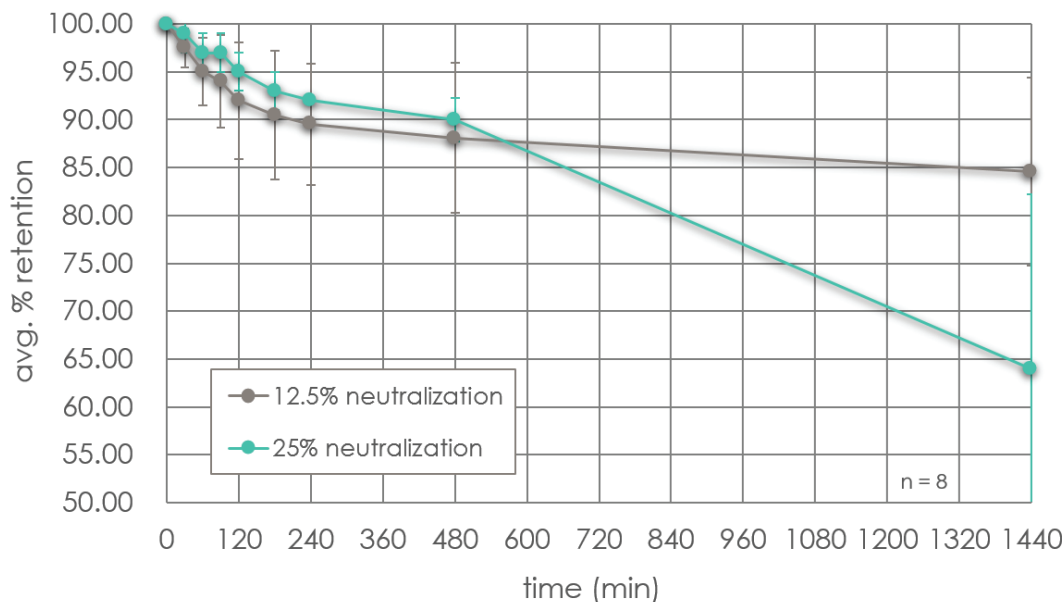
strength. Together they provide the durability for the hair spray film, the film strength and the elasticity to withstand movement without film failure. The polymer is esterified on one of the maleic acid portion of the polymer resulting in a half-ester anionic polymer. The carboxyl group is neutralizable with a recommended 15% for anhydrous aerosol hair spray applications and 10-20% for 80-55% VOC hydroalcoholic sprays. The polymer series has shown compatibility with anionic, amphoteric and

Figure 1: Chemistry



Monoalkyl esters of PVM/MA copolymer
R= ethyl, butyl, or isopropyl

Acidity:	4.0 – 5.0 meq/g or 230 -300 mg KOH/g (Acid #)
Tg:	102°C – ethyl ester of PVM/MA copolymer 72 -96°C – butyl ester of PVM/MA copolymer
Propellant tolerance:	(-30°C)
Dimethyl Ether	– 50+%
Hydrofluorocarbon	152a – 40%+
Tetrafluoropropene (HFO 1234ze)	– 40%+
Hydrocarbon	– 25%

Figure 2. High Humidity Curl Retention test of butyl ester of PVM/MA copolymer**Figure 3: Acoustical evaluation of dry hair spray films on hair**

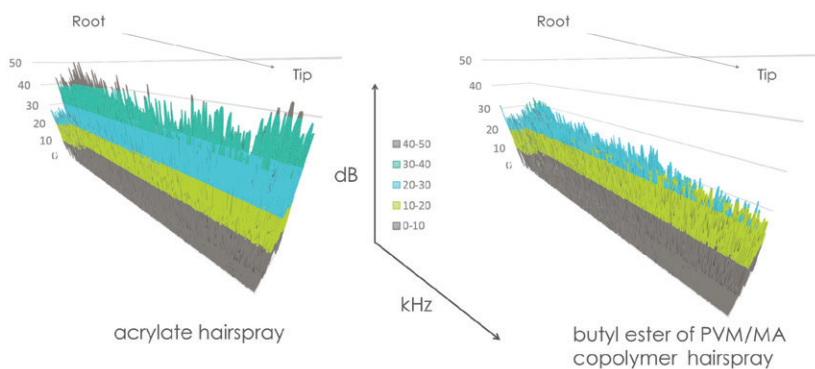
pseudo-cationic polymers to enable the formulator to create a range of hair spray formulations to meet all hair style needs.

The creation of an aerosol hair-spray requires the consideration of the entire package, concentrate, propellant and package. Interactions of these components present challenges in system and package compatibility. Esters of PVM/MA provide a range of acceptable systems including propellant variations and solvent choices. Due to the anionic contribution of the acid contribution on the backbone, water containing systems should be avoided in unlined tinplated cans. Such systems are acceptable in lined aluminum packages.

Performance: Stoichiometry

The alternating anionic moiety of the esters of PVM/MA copolymer allow for performance enhancements through stoichiometric neutralization and the types of neutralizers employed; film flexibility, hydrocarbon tolerance, water solubility and resistance can be modified to deliver desired results. Balancing the performance parameters can help to deliver the performance objectives. The butyl ester of PVM/MA copolymer can

combing acoustics demonstrate the ease of brushing vs an acrylate spray, enabling restyleability and natural feel with low residue.



deliver excellent high humidity curl retention and hold at 90% RH, though increasing the neutralization for other performance enhancements can be detrimental to its humidity resistance (Figure 2).

Hair Spray Reinvented

Hair sprays have traditionally be used at the end of the styling process to “fix” the style; to hold and protect the style from the environment such as wind or humidity, to add resiliency to compression and reduce gravity pull. Today, there is a re-invention



of the aerosol hair spray expanding its use beyond style fixation, with integration with the entire styling process and compatible with today's styling tools. This has been observed with the recent introduction of working sprays, heat styling sprays and style to finish sprays. Esters of PVM/MA copolymers meet the task as the workhorse styling polymer in these newer on-trend formulations

During the wet phase of hair styling, hair is softened and susceptible to stretching and abrasion especially during brush/blow dry styling. Therefore, protection from thermal mechanical hair damage during the styling process is critical in working sprays. Esters of PVM/MA copolymers have a lower tack phase and less grab reducing fiber fatigue during blow/dry styling and preventing cuticular lifting and stress micro cracks which can ultimately lead to the formation of split ends and hair breakage. Wet to dry styling performance is optimized.

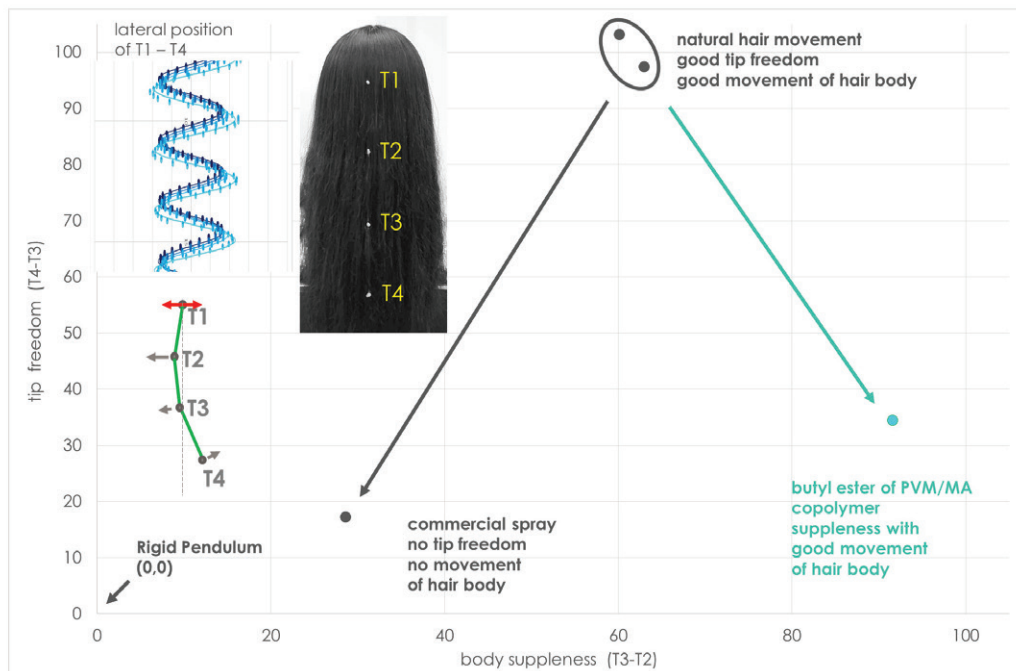
The PVM/MA copolymer backbone has demonstrated thermal protection from high temperature (450°F/232°C) thermal flat irons.¹ Thermal insult degrades hair's protein structure, reducing shine, hair manageability and natural movement. For dry hair styling with thermal tools, the low-tack phase of the polymer in aerosol spray styling formulations allows the plates of the flat iron to glide easily to prevent scorching.

During the final stage of the styling process, the polymer meets its traditional function of providing all day hold, up to 48 hours! Using one technology to achieve style, from creation to finish, delivering shine, less residue and easy to remove contrast to potential impacts of product layering.

Natural Styling

As it doesn't build up on hair with repeat application, doesn't flake and provides brushable hold, esters of PVM/MA copolymer

Figure 4. Evaluating hair movement



Movement data of butyl ester of PVM/ MA copolymer exhibits exceptional hair movement for bounce back beautiful hair.



Mannequin demonstration of Style & Creation spray.

are the perfect choice for natural textured hair. As textured hair is more fragile, the easy removability of polymer hair reduces the chance of breakage during restyling or shampooing. One consumer signal of easy brush through is sound. A novel method was developed to measure the sound of hair spray films on hair as they were broken during grooming application.² In comparison to acrylate based polymer films, esters of PVM/MA copolymer combs through easily with reduced noise providing consumer confidence of “gentler on hair.”

The film properties do not yellow on hair which allows natural gray hair to look its brightest and does not contribute to off tones for bleached blonde hair. Consumer perceivable shine benefits can be realized as well.

Hair movement depends on the properties of the individual fibers—degree of damage and wave pattern—as well as the degree of interfiber interactions. Hair sprays are good examples of high interfiber interactions often resulting in a “frozen state” with lack of movement. The increased hydrophobicity of the butyl ester of PVM/MA copolymer provides more resistance to the breakdown of the hair style and delivers improved suppleness in the body of the hair while demonstrating natural movement as indicated by the motion at the tips. A new method created while employing oscillating motion, a pendulum model can be applied to measure the movement in a hair fiber assembly. Hair suppleness can be determined by the T3-T2 measurements relative to T1. Natural movement correlates with a nonlinear behavior of movement in which tips move nearly independently from the main body.

Summary

Hair sprays continue to represent the largest share of the styling market today. Continued innovation of this format and integration with today's styling tools is key to meet the demands of the professional stylist and consumer. The digital era provides consumer's with “how to” create new styles via styling apps, video and blogs allowing consumer's to unleash their creative spirit and embrace new looks. Spray styling provides ease of use, allows the flexibility of applying product while styling and fixing the finished look.

Hair spray technologies such as monoalkyl esters of poly(methyl vinyl ether/maleic anhydride) offers the hair care industry efficient options to deliver a range of functionality in one hair spray styling product that does not limit style creativity and re-stylability for versatile style changes without the need of shampooing in between styles. Key benefits include 48 hour hold, natural hair movement, brushable hold, shine, manageability and touchable hair. Brushable hold, shine and ease of removability allows for textured hair applications whether embracing natural or the most creative updo. A perfect solution for professional hair stylist, who looks for hair styling products with performance attributes that fit a preferred hair-style of today's lifestyle, the Gantrez polymer ester series enables a new generation of multifunctional hair styling products. ●

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For more information about Ashland's Gantrez polymer ester series, visit <https://www.ashland.com/gantrez>

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Advantage™ Revive polymer brings a much-needed refresh to the dry shampoo category. This patent-pending solution delivers superior cleaning with improved sebum removal while leaving less visible residue on hair. Advantage Revive polymer improves the manageability of hair while maintaining its luster, matching the color vibrancy and shine of freshly washed hair.

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