A new polymer generation offering truly multifunctional performance

**KEYWORDS:** styling polymer for hair gels, waxes and creams, stress-strain measurements of polymer films, stiffness test, running on hand, flaking and sensory assessment

**Abstract**
Acrylates/Methacrylamide Copolymer is designed for improved hair styling performance for clear gels, waxes, creams and other styling products. In addition to its excellent styling properties, the new polymer functions as a thickener avoiding the additional use of rheology modifier. Polymer film specimens formed by dried styling gels were found to be extremely flexible. The implications of these polymer film properties on the in-use properties are discussed.

**INTRODUCTION**
After decades of development and improvement of hair styling polymers there is still room for improvement. Many generations of polymers (1, 2) have been developed over the years starting from the first synthetic styling polymer Polyvinylpyrrolidone (PVP) in the 1950s based upon a patent from W. Reppe (3). Today’s styling formulations are further optimized by the use of polymer combinations. This is especially true for styling gel and wax formulations. Combinations of styling polymers and polymeric thickeners are used to achieve the right balance of rheology profile, setting performance and humidity resistance without sacrificing sensory properties, e.g. peaking, gel structure and clarity. A lot of those formulations still contain PVP-based polymers, acrylic-based polymers and Carbomer-based thickeners. Formulations with our new multifunctional performance polymer offer an opportunity to go the opposite way and reduce the complexity of styling gel and wax formulations by the use of only one polymer. In addition this polymer also has the potential to be used in combination with non-ionic, cationic and anionic polymers to give the formulator the necessary flexibility to develop variants for differentiation of styling performance and level of hold.

**EXPERIMENTAL METHODS**

**Gel viscosity**
Gels viscosities were measured at 21°C with Brookfield RVT, sp. 7, 20 rpm.

**Gel clarity**
The transmission in a 1 cm cuvette was recorded by means of a UV-Visible Spectrophotometer, Cary 300 Scan, Agilent Technologies and by means of subjective optical assessment (clear, slightly turbid, turbid).

**Bending stiffness (4)**
The final gel formulations (e.g. formula 1 and 2) with 0.4% PEG-40 Hydrogenated Castor Oil and 0.1% perfume were diluted with water (50 g gel and 170 g water). The hair strands (glued hair strands 3.0 to 3.4 g, 20 x 2.5 cm, Kerling International Haarfabrik GmbH) were dipped into the diluted gel solution and compressed on filter paper. Afterwards the hair strands were pulled through a preparation device to ensure to align all hairs parallel to each other. Then the strands, treated with gel, were dried overnight at 20°C/65% relative humidity. Each formulation was tested on 10 hair strands to determine the average, standard deviation and confidence interval. The maximum bending force of the hair/polymer composite was measured in a tensile tester Texture Analyzer TA.XTPlus.

**Curl retention (5)**
0.9 – 1.1 g of the final gel with 0.4% PEG-40 Hydrogenated Castor Oil and 0.1% perfume is spread on a glass plate, the gel is applied with a spatula evenly on a round-shaped hair strand (tied round-shaped hair strands, 2.1 to 2.4 g, 15.5 cm, Kerling International-Haarfabrik-GmbH). Excess gel is squeezed off and then coiled around a Teflon curler. The prepared tresses are dried overnight at 70°C. After 30 minutes cooling to room temperature, the curl is carefully removed from the curler. The curls are hung up at one end, and their starting length is recorded. The determination of the curl retention is performed at 25°C and 90% relative humidity. After 5 hours, the final length of the curls is recorded. The stability of the curls in the particular climate is calculated and given in percent.

**Flaking**
Flaking is assessed by trained hairdressers on European mid brown hair strands (sewn hair strands, 12.5 – 13.5 g, 23 x 6 cm, Haarkunst GmbH Wernesgruen). The
Acrylates/Methacrylamide Copolymer is delivered as a water-based polymer dispersion with active polymer content of 30% at pH 5.5. pH values of 6.5 and higher are recommended for preparation of clear formulations. The maximum viscosity is achieved at pH 7 (Figure 1). The polymer is tailor-made to achieve maximum styling performance at a solids content of 4.0%, (Figure 2), where the viscosity is in the target range of 40 – 50 Pas (Figure 3).

Running of styling gels – ramp method
The gel flow on the hand of a consumer is simulated by a ramp. A pane of glass is used as a ramp (65°) in a closed glass container. The glass plate is covered with a filter paper drained with water and artificial sweat [6] (0.3 g of the gel is applied on the filter paper with a syringe). Now the time (sec.) that the gel needs to flow 5 cm down the ramp is detected.

Home user trials
23 users of hair waxes, gels, putties and creams performed a home user trial with a hair wax formulation containing Acrylates/Methacrylamide Copolymer (formula 3). The percentage of respondents agreeing to a statement or agreeing completely was recorded.

Water uptake of polymer films
Polymer solutions in water and final hair styling gels have been dried at relative humidities from 0 – 90% in the measuring cells of a High Throughput Sorption Analyser SPSx-1µ; Proumid Gmbh & Co. KG. The water absorption of those polymer solids was measured at equilibrium at different relative humidities (20°C).

Tensile strength and elongation of polymer films (7, 8)
Final hair styling gels with polymers, perfume and solubiliser were dried in silicone moulds. Solid specimens of the dried polymer films (34.5 mm x 6.0 mm wide by 0.13 – 0.15 mm thick) were evaluated using a Stable Micro Systems Texture Analyser TA.XTplus, Winopal Forschungsbedarf GmbH, tensile tester at 54% relative humidity and 23°C. Measured parameters were the maximum tensile strength (N/mm²) and the elongation (%) at maximum tensile strength.

ACRYLATES/METHACRYLAMIDE COPOLYMER
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Figure 1. Acrylates/Methacrylate Copolymer: Viscosity at 4.0% polymer content versus pH value (at 21°C; Brookfield RVT, sp. 7.20 rpm; mPas).

Figure 2. Acrylates/Methacrylate Copolymer: Styling performance by means of stiffness test (cN) at polymer concentrations between 1.0 and 5.0%.

Figure 3. Acrylates/Methacrylate Copolymer: Viscosities at polymer concentrations between 1.0 and 5.0% [at 21°C; Brookfield RVT, sp. 7.20 rpm; mPas]
PROPERTIES OF HAIR STYLING GELS AND WAXES

The styling performance of Acrylates/Methacrylamide Copolymer in gel formulations was compared to market standards based on PVP polymers in final hair styling formulations containing perfume, solubiliser and preservative (see Formula 1 and 2, Figure 4). The comparison was done at a total polymer level (styling polymer and thickener) of 4.0% active matter. In the case of Acrylates/Methacrylamide Copolymer there is no need of an additional thickener to achieve target viscosities of 40 – 50 Pas. The maximum bending force of the hair/polymer composite is higher in formulations with the new Acrylates/Methacrylamide Copolymer than those of conventional vinylpyrrolidone based polymers (see Figure 4). Flaking of formulations with this new polymer is significantly lower than flaking of the formulations with VP/Methacrylamide/Vinylimidazole Copolymer and PVP K 90 and on the same level as VP/VA Copolymer with low bending stiffness. The new Acrylates/Methacrylamide Copolymer can be combined with nonionic, cationic and other anionic styling polymers to increase the setting performance without sacrificing in gel sensory, rheology and clarity (Figure 5). The overall performance of those polymer combinations is on the level of market benchmarks with extreme hold. It was surprising that flaking of those polymer combinations (4.5 to 5.0 % active polymer) is even lower than in the formulation with only 4.0% of the new polymer alone. The lowest flaking was observed with the formulation consisting of Acrylates/Methacrylamide Copolymer and Acrylates Copolymer (see Figure 5).

A ramp drained with artificial sweat was used to simulate the running of gels on hand (Figure 6). Gels with Acrylates/Methacrylamide Copolymer are salt stable and do not run on the hand which is a major drawback of Carbomer based gels in combination with PVP-polymers.

Acrylates/Methacrylamide Copolymer at 4.0% polymer content can be used to emulsify a range of oils and waxes without additional conventional emulsifier to give new textures and effects. One example is given in formula 3. A home use test was performed to assess its application properties. The percentage of respondents agreeing to a statement or agreeing completely was recorded. 73% of users found the hair wax to give good hold to the hair on application. 70% found it to be easily rinsed off the hands. 83% found it to be easily rinsed off the hair. 65% found it left no residues on the hair. 65% found it made the hair easy to restyle.

MECHANICAL PROPERTIES OF POLYMER FILMS

Water uptake from pure not neutralized polymers (Figure 7) and final styling gel formulations (neutralized to pH 7, with perfume and emulsifier, Figure 8) have been measured.
un-neutralized polymer (Figure 7) but water-uptake is still significantly lower than that of Carbomer/PVP K90 gels (Figure 8). Polymer films of final styling gels with Acrylates/Methacrylate Copolymer are extremely stretchable with elongations of more than 400% (Figure 9). The polymer film from the combination of Acrylates/Methacrylate Copolymer and Acrylates Copolymer is even more elastic and the film doesn’t break at maximum stress. There is a big difference between the mechanical properties of dried styling gels based on the new anionic polymer Acrylates/Methacrylamide Copolymer and classical combinations of Vinylpyrrolidone-based polymers and Carbomer (Figure 10). Combinations of Vinylpyrrolidone-based polymers and Carbomer give much more brittle films, exhibit higher maximum tensile stress, but a very low elongation at maximum tensile strength.

**DISCUSSION OF THE BENEFITS**

The improved styling performance of the new anionic Acrylates/Methacrylamide Copolymer as the major component in hair styling gels measured on hair strands as maximum bending stiffness (Figure 4) seems to correlate well with the elongation of dried polymer films but not with the maximum tensile strength (Figure 10). For the styling performance under mechanical stress measured via bending stiffness, the elongation seems to be crucial to allow good adhesion of the polymer to the hair fibres. The cohesive properties of the polymer film measured as maximum tensile stress appear to be secondary in achieving high bending stiffness. The extreme low flaking especially of the styling gel formulation with the combination of Acrylates/Methacrylamide Copolymer and Acrylates Copolymer (Figure 5) could also correlate with the extremely stretchable film properties (Figure 9 and 10). A prerequisite for low flaking is a good adhesion of the polymer on the hair fibres. A good adhesion is only possible if the polymer has a certain elasticity avoiding breakage upon movement of the hair. The correlation of the water-uptake of films with the new Acrylates/Methacrylamide Copolymer in comparison to as a function of the relative humidity. The water uptake of Acrylates/Methacrylamide Copolymer as pure polymer un-neutralized is very low (Figure 7). In final styling gels (Figure 8) at pH 7 Acrylates/Methacrylamides Copolymer and its combination with other polymers has higher water-uptake values compared to the
PVP K90/Carbomer at 90% rel. hum. (Figure 8) with the results for curl retention (Figure 4 and 5) seems to be limited. The big difference in the curl retention is not reflected in the small difference of water-uptake at 90% relative humidity. The “no running on hand” of formulations with Acrylates/Methacrylamide Copolymer is explained by the presence of the hydrophobic monomer moiety in the polymer that lead to associative interactions occurring independently of the salt content. The stabilization of emulsions with high amounts of oils without emulsifier (Formula 3) is also explained by those associative interactions.

SUMMARY

Acrylates/Methacrylamide Copolymer provides styling properties and thickening performance for clear styling gel formulations, styling creams and styling waxes without an additional thickener and emulsifier. The new polymer has been shown to be compatible with non-ionic, anionic and cationic high performance styling polymers to give extreme styling performance and humidity resistance with reduced flaking on hair. Polymer film specimens formed by the dried gels with the new polymer were found to be flexible and pliable and did not snap or break upon bending and twisting by means of a tensile testing device. Based on our results we postulate that these film properties are important for high bending stiffness and low flaking after combing.

REFERENCES AND NOTES

1. R Lochhead, The History of Polymers in Hair Care (1940 to present), Cosmetics & Toiletries 103 (1988).
6. Synthetic Sweat: ISO 3160/2 comprising of 20g/l NaCl, 17.5 g/l NH4Cl, 5 g/l Acetic Acid and 15 g/l Lactic Acid; pH adjusted to 4.7 by NaOH).
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