Carbopol Aqua CC polymer for L

Duane Krzysik, senior R&D associate, and **Dr Krishnan Tamareselvy**, R&D associate, at **Noveon** introduce a novel cationic compatible synthetic rheology modifier for use in low pH personal care applications*

Low pH formulations are commonly defined as having an acidic (<6.0) pH or containing active acidic components. They may also contain other components, such as cationic surfactants and salts that provide additional value. Such ingredients are chosen for use in low pH formulations to treat or condition the hair and skin. Cationic ingredients can be found in shampoos and cleansing products, facial creams, lotions, gels and antiperspirants.

The formulation of stable, low pH, viscous emulsions and gel formulations with desirable aesthetics and textures is often challenging. The most commonly used thickeners are synthetic associative thickeners; these are frequently anionic and hence are typically incompatible with cationic components, especially quaternary ammonium salts. They can also be ineffective thickeners at low pH.

Formulators seeking to modify the rheology of their product compositions at low pH, especially emulsions, are limited to choosing between nonionic thickeners (such as nonionic surfactants) and cationic thickeners. The former are uncharged and thus are assumed to be less reactive to cationic components than anionic thickeners, but they tend to inactivate preservatives and may promote microbial growth.

Moreover, whilst some cationic polymeric rheology modifiers, such as hydrophobically modified aminoacrylate copolymers, are available commercially, their rheological properties are unacceptable or aesthetically unsatisfactory, yielding a 'lumpy' texture.

Carbopol Aqua CC polymer

To meet growing demand for thickeners suitable for low pH formulations, Noveon, a Lubrizol subsidiary that supplies speciality chemicals mainly to the personal care, pharmaceuticals, food and cleaning products markets, has added Carbopol Aqua CC polymer (INCI name Polyacrylate-1 Crosspolymer) to its existing Carbopol* polymer range.

The new polymer is a milky white liquid that is supplied as 20% solids, with a pH of 7.5-8.5 and a viscosity of <50 mPa·s. As a 2.0 wt% active polymer in water, neutralised with glycolic acid to pH 4.0, it has a viscosity of 11,000-18,000 mPa·s, a 2.0 wt% turbidity of <20 NTU and a yield value of 1,000-2,000 dynes/cm^2. It is comprised of:

- Amino substituents, which provide hydrophilicity and cationic properties at low pH
- Hydrophobic substituents, which moderate the hydrophilicity
- Hydrophobically modified polyoxyalkylene substituents, which provide associative properties

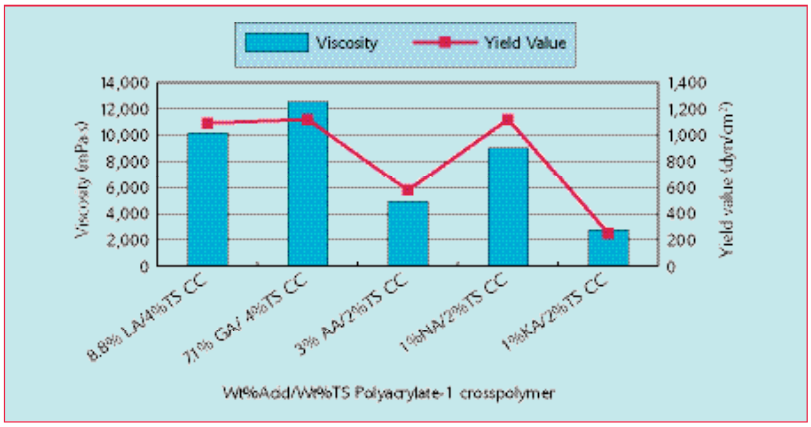

Figure 1 - Viscosity & yield of Carbopol Aqua CC polymer with different acids

- Hydrophilic polyoxyalkylene substituents, for controlled association and enhanced rheological properties
- Crosslinker

The polymer's optimised balance of hydrophilic, semi-hydrophobic and hydrophobic characters with amine functionality further activates the ionic (cationic) characteristics at low pH (in use), while also helping to build viscosity through the mechanisms of hydrodynamic thickening and controlled hydrophobic association when the pH is reduced to <6.0 through the addition of an acid.

This activates the ionic functionality of the polymer, causing the polymer to swell through charge repulsion (hydrodynamic volume expansion). Controlled hydrophobic association occurs via the combination of semi-hydrophobic and hydrophobic side chains at specific sites. Acidic ingredients used in personal care products (such as lactic, glycolic, salicylic, fruit acids and low pH salts) can serve both as active agents and acid swelling agents for the polymer to achieve the desired viscosity.

Likewise, the proprietary modified hydrophobe package also facilitates controlled associative thickening and provides enhanced rheological properties. This property clearly differentiates Carbopol Aqua CC polymer from typical associative polymers and makes it possible for formulators to create softer, smoother, more spreadable formulations with the shear-thinning rheology and suspension capabilities typical of other Carbopol polymers.

Carbopol Aqua CC polymer offers a number of important benefits, including: low pH formulation stabilisation; cationic compatibility; excellent clarity; smooth flow and shear-thinning rheology; the ability to suspend beads, capsules and powders;

Table 1 - Low pH skin care emulsions with Carbopol Aqua CC polymer: Effect of emulsifiers

Emulsifier (4 wt%)	Steareth-21 Steareth-2	Glyceryl Stearate & PEG-100 Stearate & Steareth-21	Ceteareth-25 Ceteareth-6	PEG-20 Methyl Glucose Sesquistearate Methyl Glucose Sesquistearate	Behentrimonium Chloride
Appearance & Texture	Good, low viscosity	Good, low viscosity	Good, medium viscosity, slightly fluffy (soufflé)	Good, glossy, slightly fluffy	Good & glossy
3 months @45°C, 25°C, 4°C	Passed**	Passed**	Passed**	Passed**	Passed**

** - No signs of phase separation, creaming or syneresis.

low pH skin care formulations

Table 2 - Carbopol Aqua CC polymer-stabilised glycolic acid emulsion

		INCI Name, *Trade Name*	Weight %	Function
A.	1.	Deionised Water	QS	Diluent
	2.	Polyacrylate-1 Crosspolymer (20.00 wt%), ***Carbopol Aqua CC polymer***	1.00	Rheology Modifier
B.	3.	Cetearyl Alcohol	2.00	Structurant
	4.	C12-15 Alkyl Benzoate	4.00	Emollient
	5.	PEG-20 Methyl Glucose Sesquistearate ***Glucamate SSE-20 emulsifier***	3.20	Emulsifier
	6.	Methyl Glucose Sesquistearate ***Glucate SS emulsifier***	0.80	Emulsifier
	7.	Glycolic Acid	1.00, 5.00, 10.00%	Neutraliser / Active
	8.	Triethanolamine (99.00%)	qs to pH 3.5	pH adjustment

compatibility with α-hydroxy acids (AHAs) and the acidic salts used as antiperspirant actives; versatility, via 'back-alkaline pH adjustment' in surfactant-based applications; compatibility with anionic, cationic, amphoteric and nonionic surfactants and with ethanol; and, a broad applications fit.

The new polymer is also surprisingly effective in thickening aqueous systems containing cationic ingredients (e.g. quaternary ammonium compounds, polymers and amines), surfactants of all kinds and other ingredients.

Because of all these properties, Carbopol Aqua CC polymer can be formulated into a wide variety of product forms, from non-pourable stiff to soft gels and from semi-solid pastes to substantially solid sticks, bars, squeezable gels, emulsions and roll-on products.

Use in low pH formulations

The demand for anti-ageing and skin lightening or brightening products drives formulators to look into effective ways of formulating new products with active ingredients. Some of these cosmetic actives have specific requirements to obtain desired formulation properties, such as pH and use levels.

The clinically supported ability of AHAs to impact skin keratinisation has led to their use in treating various skin conditions, including ichthyosis, acne, age spots and warts.[1] In the past 15 years, the significant anti-ageing benefits made possible through the use of AHA-containing products have helped to build the huge global skin care industry.[2]

However, AHA-containing products do have some drawbacks. The uncontrolled penetration of AHAs into the skin surface may result in burning, stinging, redness, swelling (especially in the area around the eyes), blistering, bleeding, rash, itching and skin discolouration. The irritation potential for AHAs significantly increases at pH levels under 3.5.[3]

Some formulators attempt to eliminate these negative effects, either by increasing the pH or by reducing the concentration of the acid to such an extent that the formulations are less effective than would be desirable. Since only the free acid is immediately available for penetration, it is very important to maintain the pH of an AHA-containing system near to its pKa, in order to preserve at least 50% of the bioactive acid.[4]

Thus, the remaining current challenge in formulating with AHA is balancing the efficacy, mildness and stability at formulation pH levels of 3.5-4.0. This specific pH requirement is not limited to AHA systems. It also applies to all acidic and proton-donor actives, such as kojic acid, ascorbic acid, nicotinic acid, retinoic acid and folic acid, all of which are more stable and effective in a low pH environment.[2,5]

Low pH environments also play an important role in the effective stabilisation and improved performance of cationic emulsions. These are gaining market interest, due to their exceptional skin feel, their ability to improve moisturisation levels in mature skin, and their ability to form films on the skin.

Formulating with cationic emulsifiers is not complicated, since similar techniques are used in traditional nonionic emulsification. The stabilisation of cationic emulsions is further achieved by incorporating viscosity enhancers, such as fatty alcohols, fatty acids and cationic compatible polymers.[3,4]

Carbopol Aqua CC polymer offers many benefits for low pH emulsions in the range of 2-6. Unlike many other polymers, it has a high level of acid tolerance and broad emulsifier compatibility, while providing emulsion stability and shear-thinning rheology.

Testing efficiency

The efficiency of Carbopol Aqua CC polymer in building viscosity and yield value by comparison with other rheology modifiers used in low pH applications was tested using a gel screen-

Table 3 - Skin yogurt ingredients

		INCI Name, Trade Name	Weight %	Function
A	1.	PEG-20 Methyl Glucose Sesquistearate ***Glucamate SSE-20 emulsifier***	3.2	Emulsifier
	2.	Methyl Glucose Sesquistearate ***Glucate SS emulsifier***	0.8	Emulsifier
	3.	Cetearyl Alcohol (and) Ceteareth-20 ***Promulgen D emulsifier***	1.0	Emulsifier
	4.	Dimethicone 350cSt	2.0	Emollient
	5.	Neopentyl Glycol Diethylhexanoate ***Schercemol NGDO ester***	1.5	Emollient
	6.	C12-15 Alkyl Benzoate	8.0	Emollient
	7.	Benzophenone-3	0.5	UV absorber
	8.	Ascorbyl Dipalmitate	0.5	Anti-ageing/skin lightening active
	9.	Tocopheryl Acetate *Vitamin E Acetate*	0.2	Antioxidant
B	10.	Deionised Water	57.9	Diluent
	11.	Glycerin	2.0	Humectant
	12.	Methyl Gluceth-20 ***Glucam E-20 humectant***	1.0	Humectant
	13.	Sodium Bisulphite	0.2	Antioxidant
C	14.	Polyacrylate-1 Crosspolymer ***Carbopol Aqua CC polymer***	6.0	Rheology modifier
D	15.	Glycolic Acid	5.0	AHA active
E	16.	Niacinamide	1.0	Skin lightening active
	17.	Deionised Water	5.0	Solvent
F	18.	Triethanolamine	2.5	pH regulator
G	19.	Phenoxyethanol, Methylparaben, Ethylparaben, Butylparaben, Propylparaben, Isobutylparaben	0.5	Preservative
	20.	Fragrance IFFX0588-Strawberry	0.5	Fragrance
	21.	Water (and) Sunflower (Hellanthus Annuus) Seed Oil (and) Tocopheryl Acetate (and) Retinyl Palmitate (and) Agar (and) Red 30	0.7	Anti-ageing actives

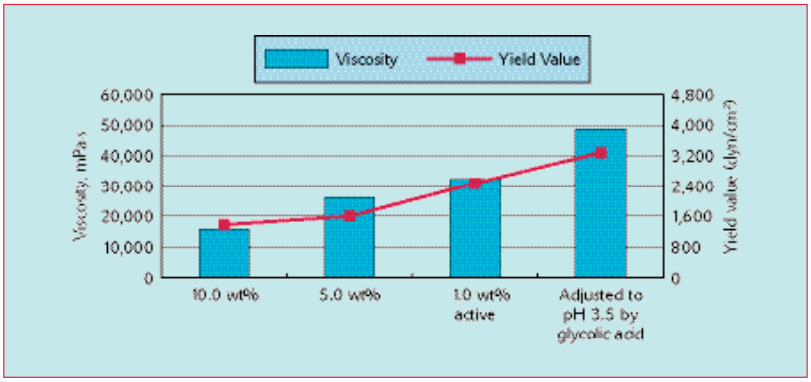

Figure 2 - Effect on viscosity & yield value of different levels of glycolic acid in a 1.0% Carbopol Aqua CC polymer skin care emulsion

ing formulation containing 2.0 wt% glycerine, 1.0 wt% methyl gluceth-20 and 0.5 wt% preservative.

Five different cosmetic acids were used to form complexes with Carbopol Aqua CC polymer: 10.0 wt% lactic acid (88%) and 10.0 wt% glycolic acid (71%), each with 4.0 wt% total solids (TS) Carbopol Aqua CC polymer, plus 3.0 wt% ascorbic acid (99%), 1.0 wt% kojic acid (99%) and 1.0 wt%, nicotinic acid (99%), each with 2.0 wt% TS Carbopol Aqua CC polymer.

The viscosities and yield values of the resulting gels were measured (Figure 1). The resulting data indicate that Carbopol Aqua CC polymer can effectively thicken acid containing gel systems in a low pH environment.

Carbopol Aqua CC polymer positively interacts with other emulsion components through hydrophobic modification, to provide synergistic viscosity and yield value even in the presence of high levels of AHA (glycolic acid). Its yield value building properties also make this material an ideal polymer for the suspension of pigments, powders, beads, capsules and the like in low pH gels and emulsions.

The co-stabilising ability of Carbopol Aqua CC polymer (at use level 1.0 wt% TS) with various emulsifiers was verified by developing six formulations based on 10.0 wt% glycolic acid and 12.0 wt% emollient emulsified with 4.0 wt% of the following emulsifier systems:

- Steareth-2 (1.0 wt%) with steareth-21 (3.0 wt%)
- Ceteareth-6 (2.6 wt%) with ceteareth-25 (1.4 wt%)
- Methyl glucose sesquistearate (1.2 wt%) with PEG-20 methyl glucose sesquistearate (2.8 wt%)
- Cetearyl alcohol (and) ceteareth-20 (4.0 wt%)
- Glyceryl stearate (and) PEG-100 stearate (2.4 wt%) with steareth-21 (1.6 wt%)
- Behentrimonium chloride (4.0 wt%)

The pH of each emulsion was then adjusted to 3.5-4.0. As Table 1 shows, Carbopol Aqua CC polymer is compatible with key emulsifier (nonionic and cationic) systems. It can be used to co-stabilise low pH emulsions and offers versatility in creating different textures to fit formulation needs. Other evaluations included viscosity, yield value and microscopic observations of the emulsions. Table 1 also shows stability results, appearance and texture for each of them.

Carbopol Aqua CC polymer's hydrophobic interaction with other components and its ability to complex with acidic actives, provides formulators with advantages when creating low pH formulations. To demonstrate this, different levels of AHA (glycolic acid) were incorporated into a screening formulation (Table 2).

For comparative purposes, all pH levels were adjusted to 3.5 prior to measuring viscosity and yield value. Figure 2 shows the viscosity and yield value that Carbopol Aqua CC polymer provides when used with different levels of glycolic acid. This interaction offers considerable formulation flexibility at low pH levels.

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Formulating with Carbopol Aqua CC polymer

Recommended use level of Carbopol Aqua CC polymer is 0.5-2.0 wt% solids (2.5-10 wt% as supplied) and the recommended pH level is <6.0; optimal viscosity and clarity are achieved at pH 4-4.5. Neutralisation can be achieved with carboxylic acids (glycolic acid, lactic acid, citric acid, etc.). The recommended surfactant active use levels for cleansing systems is 8.0-22 wt% active or as needed for desired levels of foaming, viscosity and clarity.

Carbopol Aqua CC polymer is used as a stabiliser in a number of low pH formulations. An example is a nourishing skin yogurt (Table 3) that is formulated with AHA and methyl gluceth-20 and fortified with different vitamin derivatives to promote lighter, younger looking and softer skin.

A low pH emulsion, it features a primary emulsifier system that is a glucose-derived combination of mild nonionic emulsifiers (Glucamate* SSE-20 and Glucate* SS, co-emulsified with Promulgen* D). The formulation also contains Schercemol* NGDO ester to mask the tackiness and stickiness of AHA.

To formulate the skin yogurt formulation, first heat parts A and B in separate vessels to 70°C, with mixing. With both phases uniform, slowly add part B to part A using moderate agitation. When the batch is uniform, gradually cool to 55°C with continued mixing. At 55°C, add part C (Carbopol Aqua CC polymer). As gradual cooling and mixing continues, add part D (glycolic acid) and pre-mixed part E and adjust pH to 3.5-4.0 with part F (triethanolamine). When the batch reaches 45-50°C, add part G ingredients one at a time with mixing. Continue cooling and mixing until completion at 35-40°C.

Conclusion

Carbopol Aqua CC polymer facilitates the formulation of stable low pH gels and emulsions that have a yield value suitable for the suspension of powders, beads and microcapsules. It offers shear-thinning rheology and smooth feel in applications.

It is also compatible with low pH actives like AHAs, vitamin acids (L-ascorbic acid and L-nicotinic acid) and skin whitening actives (such as kojic acid). These cosmetic acids can be used to neutralise Carbopol Aqua CC polymer to the desired low pH where these materials can provide efficacy.

Carbopol Aqua CC polymer has also been found to interact positively with fatty alcohols and other fatty cosmetic ingredients through hydrophobic interaction to provide synergistic viscosity and yield value enhancement. Finally, it is compatible with cationic ingredients that can provide improved skin feel and increased skin moisturisation in low pH emulsions.

Thus, Carbopol Aqua CC polymer is suitable for the development of a wide variety of skin care products including: skin lightening or brightening formulations; masks (hydrating and skin lightening masks); anti-ageing and exfoliation formulations; skin tone correctors (foundation bases); and, sunscreens and UV protection formulations.

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For further information, please contact:
Noveon, Inc.
9911 Brecksville Road
Cleveland
OH 44141-3247
US
Tel: +1 216 447 5000/+1 800 379 5389
Websites: www.personalcare.noveon.com