Géraldine Bernard, Lucile Blain, Virginie Boulier, Manuel De Arriba, Pamela Eklou – Sensient Cosmetic Technologies, France

Applications of acrylic polymers and copolymers

For many years, the cosmetic industry has been looking for revolutionary products to offer innovative concepts to its consumers. Cosmetic ingredients such as acrylate polymers and copolymers help to create various formulas with different visual and sensory effects (mattifying, soft, ball-bearing, velvet feelings, etc.). This article will look at acrylic polymers and copolymers in both liquid and powder form, focusing on these texturing agents as beads, thickeners, film-formers, associative polymers and more.

Beads

Solid polymers such as PMMA (polymethyl methacrylate) were introduced into cosmetic products more than 20 years ago. New technologies have been developed to achieve very innovative products, with versatile properties and applications. A composite material including silica will also be discussed.

Our review focuses on polymers based on methyl methacrylate monomer which has a spherical shape. By controlling the process and the cross-linking polymerisation, various derivatives can be obtained: different sizes, variable porosity, optical properties, etc. Table 1 and Table 2 show the leading products in the market, which are classified according to their porosity and particle size. We will review in succession the non-porous and then the porous beads. Various types of beads are available on the cosmetic market, including the Covabead range developed by Sensient Cosmetic Technologies.

Non-porous beads

Polymethyl methacrylate (PMMA) is obtained by suspension polymerisation into spherical beads from methyl methacrylate monomer. In Covabead (now referred to as 'the cosmetic bead') PMMA, the residual monomers are removed by high purification.

These 10-micron beads provide smoothness and fluidity to cosmetic products and a transparent effect on the skin. As with all PMMA beads, it has soft focus properties. A soft-focus product can be defined as a material having a high Haze Index (good transparency, with a maximum of diffused transmitted light) resulting in a blurring effect.

Cross-linked polymethyl methacrylate achieves interesting physical and chemical properties. The cosmetic bead MMC (7 microns spheres) is a type of polymer that imparts high resistance in organic solvents, allowing its use in nail varnish (hardening and mattifying effects). The suppleness of this structure and the low absorption of oil makes it a good binder for pressed powders.

A unique patented technology has been developed recently to achieve a cross linked polymer (the cosmetic bead Velvet 20) with perfect spherical shape and extremely mono-sized big particles (20 microns). They are completely transparent on the skin giving a super ball-bearing effect, velvet touch and volume in mascaras. Since they are non-porous, they do not dry the skin, absorbing moisture and sebum making them ideal for dry, normal and sensitive skin.

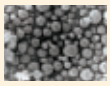
Recent technologies have achieved innovative composite products which have multiple functions. The cosmetic bead PMMA 2MUSI is a composite material made of spherical PMMA beads of 8 microns including small silica beads within the structure. This composite provides a unique soft focus effect. These properties will be used in all kinds of skin care products (gels or emulsions) to cover wrinkles and fine lines. It also acts as pore minimiser. Solid spherical acrylic polymers offer a very wide range of performances and cosmetic properties. They are versatile compounds which can provide unique

Table 1: Plain ultra-fine spherical beads.

Properties	Covabead MMC	Covabead PMMA	Covabead PMMA 2MUSI	Covabead Velvet 20
Electron micrograph				
Average particle size	5-7 µm	10 µm	8 µm	20 µm
Average specific area	1 m^2/g	1 m^2/g	2 m^2/g	0.6 m^2/g
Average forced mineral oil absorption*	0.7g/1g	0.8g/1g	0.75g/1g	0.6g/1g
Average forced water absorption**	0.6g/1g	0.7g/1g	0.6g/1g	0.6g/1g

*Sensient's method 10-204 **Sensient's method 10-146

Table 2: Hollow ultra-fine spherical beads.

Properties	Covabead LH 85	Covabead LH 170	Covabead LH70-3
Electron micrograph			
Average particle size	10 µm	10 µm	3 µm
Average specific area	85 m^2/g	170 m^2/g	70 m^2/g
Average forced mineral oil absorption*	1.3g/1g	2.4g/1g	1.4g/1g
Average forced water absorption**	1.6g/1g	2.3g/1g	1.7g/1g

*Sensient's method 10-204 **Sensient's method 10-146

textures, soft feel on the skin and optical effects to achieve innovative formulations for make-up and skin care.

Porous beads

These materials are cross-linked polymethyl methacrylate. Pore size and specific area are adjustable through an innovative controllable polymerisation process. The spherical beads have very high specific area ranging from 85 m2 (i.e. LH 85) to 170 m2 (i.e. LH170). They have a strong capacity for water and oil absorption, providing interesting and innovative cosmetic applications.

The LH85 grade has a slow absorption capacity, whereas the LH170 and LH70-3 grades have a much faster one. They absorb sweat and sebum, resulting in a dry and matte effect on the skin. These powders prevent shining of the skin by utilising light scattering on the sphere surface. This gives the effect of optically suppressing makeup smudging. They also impart a powdery feel to oily products and they prevent the sticky skin feel after the application of a water-based gel.

The high porosity of these beads transforms them into an efficient delivery system. They can be loaded with various oil or water products and they protect the formula from the loading liquid. The load is then released when applied on the skin. A perfume in powder form is one example of innovative formulation. This revolutionary concept can also be applied to skin care formulas to provide soft touch, good slip, soft focus and instantaneous matte effect (Formulation 1).

Thickeners

Acrylic acids are polymers produced from acrylic acid which is obtained from propene, a byproduct of ethylene and gasoline production:

$$CH_2 = CHCH_3 + 1.5\ O_2 \rightarrow CH_2 = CHCO_2H + H_2O$$ [1]

These polymers are easy to produce, very stable and with good safety for the skin. Cosmetic grades have controlled[1] monomer content and very good microbiological purity. Acrylic acid polymers are water dispersible in acidic conditions and their dispersion thickens with the increase of pH: acrylic acid functions $(CH_2=CH–COOH)_n$ turn to acrylate $(CH_2=CH–COO^-)n$ negatively charged inducing electrostatic repulsion. The high repulsions uncoil long molecules leading to an increase of viscosity.[2]

Acrylic polymers exhibit different properties depending on their chain length, their degree of crosslinking and the nature of their crosslinking agent. Thanks to the broad range of available grades, acrylic polymers exist for many different applications (Fig. 1).

Linear acrylic polymers with short chain length are water soluble and they are used for their metal quenching properties.

Acrylic acid polymers such as Covacryl AC with a longer chain are water dispersible and lead to transparent stringy gels such as 'spider web' hair gel. When picked up with fingers, the gel elongates. These kinds of polymers are highly efficient in elongating mascara by placing mascara formulation at the end of eyelashes for an increase of length. Their skin feel is very slippery with a very long play time. In another application, a slurry of linear polymer can be gelified with alumina and molded in a special shape for a patch such as an anti-ageing, moisturising or refreshing patch for tired eyes.

Slightly cross-linked acrylic polymers are used to formulate transparent, non stringy gels for skin care and make-up. Their skin feel is natural with a short play time often required for creams that should penetrate fast. Depending on their chain length, they can thicken water. Some high chain length medium cross-linked polyacrylates are very sensitive to pH and to salt. They can react with the salt and pH of the skin to instantaneously lose their viscosity when in contact with skin. This property is very useful for applications such as a makeup remover cream that turns into a lotion once applied on the skin.

Highly cross-linked polymers are the new players in the formulation of beauty products. MV40 & MV60 from Sensient Cosmetic Technologies are revolutionary polymers since they are in-between powders and thickeners. Indeed, because of their very high degree of cross-linking, they do not uncoil when dispersed in water. They only swell in water due to hydrogen links and to osmotic pressure leading to an increase of viscosity. Because there is a little less possibility of electrostatic repulsion, MV40 & MV60 are a little less sensitive to pH and to salt. Their skin feel is velvet powdery and dry fresh. Swollen particles slip on the skin like water-based silicone elastomer giving a premium skin

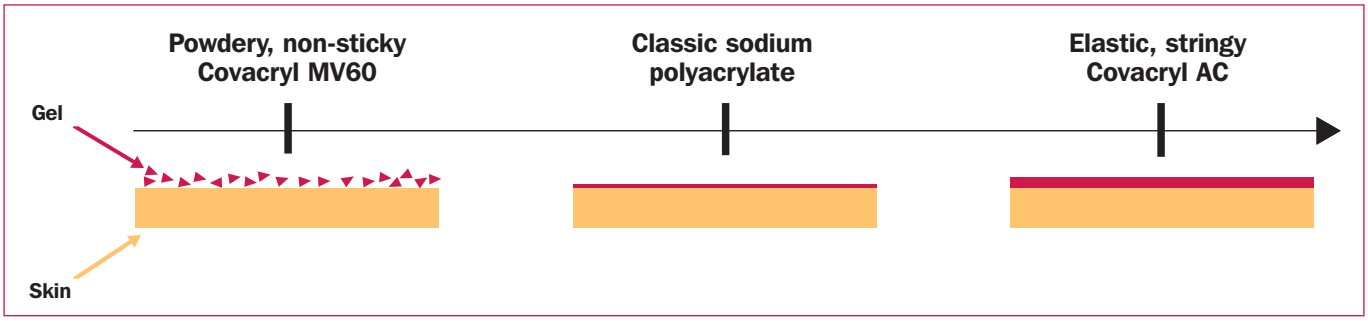


Figure 1: *The different properties of acrylic polymers depending on their structure.*

feel to aqueous serum and oil-in-water emulsion. Depending on their particle size, resulting formulations are more or less matte. MV60 gives a matte visual aspect to creams.

Our R&D laboratories have developed a new grade with a smaller particle size, MV40 for more satin formulations. These polymers are very easy to use. When introduced in water, the frosted-like gel exhibits a nice bouncing texture. Once on the skin, the water-swollen powder liberates water slowly for a long, fresh skin feel. When introduced in a water-in-oil emulsion, these polymers impart a velvet skin feel. The dry and matte skin finish is highly appreciated for men's skin care products (Formulation 2).

These polymers can also be associated with hydrophobic particles for formulations of creams with a 'mousse au chocolat' texture containing up to 95% water. Last but not least, these polyacrylates associated with hydrophobically-coated alumina can be used for formulation of creams-in-powder form. These loose powders containing up to 85% water contain particles of polymer filled with water. These swollen particles collapse during application on the skin, liberating the water.

Acrylic acid polymers are one of the

basic ingredients in cosmetic formulations, and today they are manufactured via a synthetic process. In the future, however, natural origin acrylic polymers obtained from sugars will be available for greener formulations.

Acrylic copolymers

A film-forming agent is used to obtain a continuous film on the skin, hair or nails. Their characteristics enable usage in several applications including nail polish, eyeliner, mascaras, lipsticks, liquid makeups, sunscreens and skin care products (lotions, creams, etc.). To obtain a film, ingredients such as waxes, resins, gums, cellulose and its derivatives or polyquaterniums can be used in formulations. And if acrylic copolymers have been described as beads or gelling agents, they can also show film-forming properties.

To become film-formers with defined softness, water resistance and hardness, acrylic monomers as acrylic acid are copolymerised with a second monomer. This other unit can be a methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate or an isobutyl acrylate. The choice of the monomer, the ration and the process will be monitored to design film-formers.

The film-formers can be soluble in the oil phase such as silicone acrylate copolymer or in the water phase such as acrylic copolymers; the choice of the phase depends on the desired application and benefits. They can be more or less flexible; this state is explained by their glass transition temperature. Indeed, the glass transition temperature, noted Tg, characterises the flexibility of a polymer. Below this temperature, the polymer forms a hard and glossy film. These copolymers with high glass temperature enable the formulation of long lasting cosmetic products. The film forming is more adhesive on the substrate and not sticky after drying. Above this temperature, the polymer is

more soft and flexible. Low glass temperatures make formulations more supple.

Silicone acrylate copolymers, which are graft copolymers with an acrylic polymer back bone and a silicon side chain, are used in the oil phase. Silicone acrylate copolymers form flexible films with excellent water and oil repellency. Also, they are excellent film-formers, providing long lasting properties. These properties are useful for long lasting sunscreens, while in lipsticks it pairs with an excellent sensory profile, translating into improved non-transfer while maintaining very good wearing comfort. They also are permeable to water vapour, so they do not interfere with skin exchange function, an important parameter for products designed for a long lasting wear. Cosmetic products have minimal tackiness and greasiness, leaving the skin smooth, without a dry after-feel. For easy formulating, the silicone acrylate copolymers are compatible with a variety of common cosmetic ingredients, including pigments and organic sunscreens. The formulation with silicone acrylate copolymer showed significant improvement in shine, ease of application, nourishing skin feel and comfort.

Film-forming acrylic copolymers are ideal for water-based cosmetics that require a water resistant film with an excellent abrasion characteristic. They have a good substantivity, and a more or less high gloss, depending on their grade. Typically, these water resistant films are permeable to moisture and oxygen creating a 'breathable' barrier that can be easily removed with soap and water leaving no build-up of polymer on the substrate. They give non-transfer properties, that is to say a film-fixing pigment, powder or even coloured fibre on skin, hair or eyebrows.

In 2012, Sensient Cosmetic Technologies launched a new acrylate copolymer emulsion containing a polar group, Covacryl MT10, an ethylhexyl acrylate copolymer, that forms a supple and stretchable film (because of its low glass transition temperature of 13˚C) with a good water resistance. This material can be used in colour cosmetics as a coating film-forming agent for eyeliners, mascaras or nail enamels or for skin care products, or even for innovative texture as aerosol peeling formulations. Its tightening properties form a natural-feel, supple and stretch resistant film, ideal for patches in a liquid or gel form (Formulation 3).

Film-forming acrylic copolymers have the ability to be compatible over a wide range of pH, salt, alcohol and a lot of thickeners, enhancing the variety of applications. From soft to hard flexible films, film-forming acrylic copolymers can be used alone, in combination with one another or with acrylic thickeners, enhancing the ability of the formulator to produce water-based, long wearing makeup and skin care products with unique textures.

Formulation 1: Skin care in powder form NG. **TW1899**

Phase	Trade name	INCI name [EU]	%W/W
A	Alumina AS-EM[1]	Aluminum hydroxide, triethoxycaprylylsilane	5.00
	Talc AS R0435[1]	Talc, triethoxycaprylylsilane	9.00
	Covapearl Pink 433 AS[1]	CI 77891, mica, triethoxycaprylylsilane	2.00
	Covabead LH 70-3[1]	Methyl methacrylate crosspolymer	2.00
B	Pure water	Aqua	69.40
	Covagel[1]	Sodium carboxymethyl starch	3.00
	Glycerin	Glycerin	8.00
	Phenoxyethanol	Phenoxyethanol	0.30
	Fucosorb WP[1]	Algae extract, sorbitol, aqua, potassium sorbate, sodium benzoate	1.00
	Citric acid	Citric acid	0.30

Procedure: Blend all ingredients of phase A except pearl in a coffee mill 30 seconds. Add pearl and mix for two seconds. Add Covagel to the rest of phase B under stirring. Stir for at least five minutes. Add phase A on phase B at once and stir with a 5-blades propeller for at least 5 minutes at 600 rpm.

Formulation 2: Eye wake-up gel for men. **TW1937**

Phase	Trade name	INCI name [EU]	%W/W
A	Pure water	Aqua	95.1
	Preservatives[2]		0.3
	Glycerin[3]	Glycerin	2.0
B	Covacryl MV 60[1]	Sodium polyacrylate	1.5
C	Covabead PMMA 2MUSI[1]	Methyl methacrylate crosspolymer, silica	1.0
D	Natpure UV SORB[1]	Sucrose laurate, Sucrose dilaurate, Sucrose trilaurate, glycerin, Camellia sinensis extract, Centella asiatica extract	0.1

Procedure: Prepare phase A. Add phase B under stirring. Add phase C under gentle stirring. Add phase D under gentle stirring.

Formulation 3: Patch in gel form. **TW1601C**

Phase	Trade name	INCI name	%W/W
A	Cova B Trox	Magnesium gluconate, Algae, Cichorium intybus root extract, Maltose	2.40
	Monopropylene glycol[4]	Monopropylene glyco	4.00
	Covacryl RH	Synthetic beeswax	0.80
B	Pure water	Aqua	67.30
	Preservatives[2]		0.30
C	Covacryl MT10	Acrylates/Ethylhexyl Acrylate Copolymer	25.00
D	Fragrance		0.20

Procedure: Disperse Cova B Trox + Covacryl RH in Monopropylene Glycol. Add phase A to phase B under mechanical stirring. When homogeneous, add phase C to A+B. Add phase D.

Suppliers: 1 Sensient Cosmetic Technologies 2 Thor Specialities 3 Ami 4 Mosselman

Conclusion

Acrylic polymers and copolymers are broadly used in the cosmetic industry in all kind of applications due to their stability, chemical purity and high technology. Nevertheless research and development of the beauty industry is still in search of breakthrough technologies. We can imagine the future years with new structures for these texturing agents to provide many new other properties. PC

References

1 Leroux P. Acide acrylique. In: *Fabrication des grands produits industriels en chimie et pétrochimie*. Techniques de l'Ingénieur 1993; 15-6.

2 Benedek I. *Pressure-sensitive formulation*. AH Zeist, The Netherlands: VSP 2001; p518. ISBN 9067643300.

3 Boulier V *et al*. *Use of small particle size cross-linked copolymer of acrylic acid and sodium acrylate in skin care and make-up*. Covacryl MV series RD505019 April 2006.