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Hair-raising

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Silicone elastomers as novel plasticisers

Michael Mosquera and **Juan Mateu** of **Alzo International** introduce a novel plasticser system for cosmetics*

Plasticisers improve the performance and versatility of plastics in the automotive, coatings and adhesives and construction industries. Although over 500 plasticisers are available globally, only about 50-100 are used for commercial purposes.[1] About 90% of their use is in PVC production, most of the rest with synthetic rubbers, cellulosics and acrylics.[2]

Plasticisers are also commonly used in cosmetics, where their flexibility in formulating products that in turn feeds the continuous demand for new products. This article will introduce a novel plasticiser system for multi-functional applications in personal care

What is a plasticiser?

Surprisingly, there are several definitions of the word 'plasticiser' depending on the application and end use. The ASTM defines a plasticiser as a substance incorporated into a plastic to increase flexibility, workability and distendibility, while Moxie International's Glossary of Concrete Terms describes it as a material that increases the workability or consistency of a concrete mixture, mortar or cement paste.[3,4]

The Rubber Glossary refers to a plasticiser as a substance, usually a heavy liquid, added to an elastomer to decrease stiffness, improve low temperature properties, and improve processing.[5] Finally the medical definition is a chemical added especially to rubbers and resins to impart flexibility, workability or stretchability.[6]

The common thread is that a plasticiser changes plastics to provide flexibility and increases their uses in different manufacturing conditions and processes. Plasticisers are typically liquids, inert and with high boiling points and low vapour pressure.

In addition, they act as a 'spacer' between molecules, increasing the intermolecular spacing of a plastic and decreasing the cohesive intermolecular bond, thus making the material softer and flexible. This softening is shown by the decrease in the material's glass transition

The elastomer dispersion acts as a 'spacer' in the thermoplastic

temperature (Tg) as the level of plasticisers increases

For the most part, plasticisers are organic liquids, including petroleum, coal tar distillates, animal fat derivatives, plant extracts, etc., and reactive products made from them. Esters are the most popular type and can be formulated to meet specific plasticising needs, the commonest sub-type being phthalate esters because of their low cost and good performance.

The majority of the most effective plasticisers are those which are not reacted with the thermoplastic polymer but interact physically with it. They are also for the most part considered external or physical plasticisers; an internal plasticiser denotes the chemical bonding of a plasticiser onto an elastomer.

Use in cosmetics

In addition to softening the polymer, plasticisers lower the processing temperature, reduce mixer and mould sticking, increase cohesion and improve surface appearance and wetting. These benefits are no less important to modifying and improving the overall performance of finished formulations applied to the hair, skin and body.

Basic cosmetic formulations, such as lipsticks, almost always require a plasticiser, such as an ester or oil, to soften the waxes in order to improve the overall adhesion of the product to the lip. Resins used in hairsprays and nail polishes have traditionally used solvents, again including esters and oils, to make the polymers flexible, less brittle and easier to apply and to improve overall adhesion. Internal plasticisers are also used to impart different physical attributes of the resin in solution.

Phthalates esters have been banned from use in cosmetics due to the risk of their being absorbed through the skin or inhaled and causing damage to the liver, kidneys and lungs. Therefore, there has been ongoing interest in finding plasticisers that are effective and, most importantly, safe for use in personal care products.

US-based Alzo International has recently discovered that silicone elastomers act as plasticisers in water-based or water-dispersed thermoplastics. These elastomers impart flexibility in a film by creating spaces between the molecules of the thermoplastic.

The spaces soften the polymer, which reduces the viscosity of the thermoplastic and aids in the diffusion of the polymer onto and into a substrate. This diffusion creates better adhesion due to its increased contact or wetting of the surface and reduces voids in the adhesive/ substrate interface, thus increasing the contact points.

As the thermoplastic dispersion dries, the elastomer acts as 3D 'spacers' in the plastic to create a flexible and durable film (*pictured above*). The thermoplastic elastomer (TPE) is now 'anchored' into and onto the silicone thermoset elastomer, while all the other ingredients are 'anchored' into and onto the film created by the NuPLastic film system.

When using a typical plasticiser, such as an ester that is held in place by the thermoplastic liquid, exudation is not to be expected and is not desirable. In addition, these esters will soften and lose cohesion due to a lowered Tg. Under certain conditions of time, heat, microwave or choice of plasticiser, exudation will occur, resulting in poor film quality.

In contrast, the new NuPLastic system eliminates or minimises the negative impact of the addition of a mono-functional plasticiser, actually enhancing the strength of the film formed. It results in water- and transfer-resistance qualities that lead to a long-lasting film formation.

Silicone elastomers are commonly used in cosmetic compositions for various functions but primarily to provide an emollient feel. They are rarely used or associated as plasticisers for a water-based or water-dispersed thermoplastic resin or adhesive.

The silicone polymers are composed of repeating dimethylsiloxanes units, which may be terminated in various ways. These terminations, in large measure, determine their properties (i.e. hydrophilicity) and their ability to react with other materials.

In addition to the terminal groups, the polydimethylsiloxanes themselves can have widely varying molecular weights and may be linear, branched or cross-linked structure. Each of these variations will produce widely varying properties and uses. The selection of a functionalised silicone elastomer allows an extremely water-resistant film to hold and deliver water- or oil-soluble ingredients onto the substrate.

These highly cross-linked silicone polymers have physical properties that resemble those of rubber. They deform and stretch when force is applied, bounce when dropped to the floor and show an elastic memory, i.e. exerting a force to return to their original shape once they are deformed. When diluted or dispersed in a solvent or liquid, they find use as film-forming materials.

Furthermore, when used in cosmetics or personal care products, the elastomer solutions or dispersions produce a very smooth, non-oily, dry-feeling lubricity on skin and hair. This effect is especially appreciated in make-up products that contain pigments, because product application is greatly improved and the elastomer film can reduce the rubbing-off of the pigments once the product has dried.

The silicone elastomers of particular interest are the NuLastic range, which are cross-linked as a solution in low viscosity silicone oil, hydrocarbon oil, a cyclomethicone or mixtures thereof, featuring alkyl chains for better compatibility with organics compounds including actives. They also include NuLastic Surf elastomers which have ethoxylated chains and so allow for emulsification.

These silicones have a cage-like or scaffold structure. Cross-linking gives them their solvent-gelling ability. Compatible solvents, which include volatile compounds like cyclopentasiloxane and isododecane as well as cosmetic esters and oil, occupy the spaces formed by the cross-linked structure. This results in a swelling of the 3D cross-linked silicone structure.

Lip glosses with (a) & without (b) silicone elastomers as plasticisers

Silicone elastomers also tend to be very cohesive. The less solvent, the more cohesive the molecules are. This cohesiveness is evident in the ability of this type of material to form films on the skin. These films are known to resist transfer. The cohesion of the silicone elastomer holds the film and ingredients included in a composition on the skin or hair.

A film created solely by a cross-linked silicone elastomer, will produce a discontinuous film. Once this film is applied to the substrate, it cannot removed in one or several pieces, only by wiping away. Water-based thermoplastic resins form continuous films, which can be peeled away in parts or in their entirety.

In essence, a typical thermoset silicone elastomer and thermoplastic resin exhibit characteristics which are quite different from each other. This fact suggests that such a combination would have mediocre, if not poor, combined film characteristics, because the attributes would work at cross purposes to each other.

Unlike other silicone elastomers, Alzo's have film-forming, emulsifying properties, as well an amine functionality, allowing for enhanced solubility of both hydrophilic and lipophillic properties.

In addition, cationic charge elastomers create outstandingly durable films that are ideal for blending water-based thermoplastic resins and achieve a compositional result far superior to past attempts at creating long lasting, water- and transfer-resistant films. The elastomer can also aid in pigment dispersion and has increased compatibility with hydrocarbons and silicone-type ingredients.

A silicone elastomer combined with an emulsifier would enable water-based materials to be used in emulsions. Both materials would have to be soluble and/or compatible with thermoplastic resins. Compatibility ensures that a homogeneous film is formed. This is critical in maintaining proper adhesion. Just as important, cohesion would be maintained.

As indicated before, most water-dispersible thermoplastic resins tend to be low in viscosity. This means optimised diffusion into the substrate, in turn leading to better adhesion and better film attributes. The use of the silicone gels as plasticisers and emulsifiers would actually function as a thickener and add viscosity, not reduce viscosity as in the case of esters.

All this allows for colorants, like pigments and pearls, and actives in solid form to be used at high levels without settling to the bottom of the package. The higher the level of silicone elastomer, the greater the viscosity of the emulsion; therefore the variety of product forms increases. This is an obvious additional benefit for use in pigmented make-up and lip products.

Thermoplastic resin has been found, when combined with an elastomer in this system, to cast a film that stretches. Adding more elastomer to the composition provides even greater stretch to the film, whereas reducing it likewise reduces the stretch and flexibility of the film. This too can be a very desirable property for use in topical applications.

When using an elastomer with a non-volatile carrier, such as isononyl isononanaote, the ester is entrapped within the voids of the polymer, allowing for the loading of up to 50% of a lipophilic material. This results in an outstanding emollient film that is highly desirable when applied to the lip or skin.

In addition these entrapped oils add shine, sheen and lubricity. The entrapped ester is subject to exudation, allowing for the extended and prolonged delivery of the emollient which further adds to the system's sensory appeal. Conventional liquid ester plasticisers do not exude from the thermoplastic, resulting in films that tackify. This high loading of oils would also allow for the entrapment of fragrances and other olfactory compounds, further enhancing its utility in personal care and cosmetic products.

The blend of thermoplastic resin and elastomer often contains a volatile solvent, which evaporates or becomes absorbed into the skin. Drying times may vary as a function of the volatility of the volatile solvent, its boiling point and vapour pressure. Often, a film will be dry after application to a keratinous surface, such as the skin, within about three to five minutes.

The silicone elastomers, gelled in most cases in volatile solvents, set in a matter of seconds and can be considered dry after application to lips or skin, unlike other film formers which may require five to ten minutes to dry. This is obviously another highly beneficial feature of their use as plasticisers

Another is the ability to develop transfer-resistant products, which are typically associated with colorants, such as pigments, pearlescents, dyes, etc., in mascaras, lip products, eye shadows, blushes and foundations. A visual transfer of colour from a first substrate to a second, such as the lip, face or skincare formulation, denotes a failure of the film and leads to an undesirable decrease in wear properties.

The films prepared from the new silicone elastomers exhibit transfer resistance compared to prior art films and do not transfer appreciable quantities of colour to a second substrate. Colourless products are not generally regarded as transfer-resistant so much as water-resistant. This implies transfer resistance but is not physically identical. The product is made water-resistant so that the actives do not transfer from the applied area.

In these respects, the use of these silicone elastomers as plasticisers contributes to 'long wear', in which the film maintains its integrity on the surface to which it has been applied. The longest wear claims for marketed lip products are currently up to 16 hours. The photos above show the transfer-resistant properties of the silicone elastomer in lip gloss by comparison with a conventional lip gloss.

Summary

NuPLastic films have been shown to be transfer- and water-resistant thanks to the use of the silicone elastomer plasticiser and also superior to other commercial film formers used in cosmetic and personal care products.

This patent pending system is not product-specific, so it allows users to customise specific film blends based on the selection of the specific silicone elastomer, for example using a volatile or non-volatile solvent, or having emulsification properties or a cationic charge and thermoplastics which will result in films with specific features and benefits for use in personal care products.

* - Also contributing to this article was Michael Batko

References

1. Plastemart.com, An Overview of Plasticisers and their effects on Human Health and Environment, April 14, **2008**
2. D.F. Cadogan & C.J. Howick, Plasticisers in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim **2000**, doi: 10.1002/14356007.a20_439
3. ASTM D883, Plastics Nomenclature
4. Moxie International, Glossary Index for Cement and Concrete Industries (www.moxie-intl.com/glossary.htm)
5. S.R. Pluchinsky, Rubber Glossary, Babylon Information Platform
6. Merriman-Webster Medical Dictionary

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