Nanoparticles in Cationic Radiation Curable Silicones : Examples in Nanocomposites, Hard-Coatings and Conformal Coatings

JM. Francès, V. Hantin, S. Schneider

BLUESTAR SILICONES Centre de Recherches et Technologies
85, Rue des Frères Perret
F-69192 Saint-Fons, France
sophie.schneider@bluestarsilicones.com

ABSTRACT

Cationic Radiation curable silicones are used in many applications because of the intrinsic properties of silicones combined with the process and productivity advantages of the UV cationic technology.

To achieve high performance, especially high mechanical properties, without the lose of transparency required for UV curing, one solution is the addition of nanoparticles in our formulation.

Three examples illustrating these works are presented: nanoparticles in UV Hard-Coatings, in Biomedical Composition and in Conformal Coatings.

Keywords: colloidal silica, UV curable, silicones, mechanical properties, hard-coating, conformal coating

1. INTRODUCTION

Silicones have become a very important polymer for key industry such as Electronic, Automotive, Personal Care, Textiles, Coatings and many others. Their properties: thermal resistance, hardness, flexibility make them interesting especially for coatings industry. Cationic Epoxy Silicones are recommended for release coatings applications, electronic or optical coatings. Due to their biocompatibility and very low shrinkage they are also used for some biomedical applications (adhesive, composites…).

In order to get new opportunities for such materials, some of the properties and especially the mechanical properties have to be improved without affecting the others (viscosity of the system before cure, opacity…). The nanoparticles appear as good candidates for formulation of new products with enhanced performance.

Bluestar Silicones has performed such formulation work with Cationic Radiation Curable Silicones and colloidal silica. One important parameter is to manage the transfer of such colloidal silica in the Silicone matrix. Three illustrations are described in this paper:

- the use of colloidal silica in solvent, in UV Silicone Hard Coat to match the performance of Thermal Silicone Hard Coats,
- the use of colloidal silica in cationic reactive diluents to improve mechanical properties of Biomedical Composition,
- the use of nanoparticles to improve hardness of Conformal Coatings.

2. CATIONIC RADIATION CURABLE SILICONE

At the moment, there are at least two categories of photocurable silicones. Functional silicones which cure by free radical processes such as acrylates, or vinylethers and functional silicones which cure via cationic processes such as epoxies or alkenylethers.

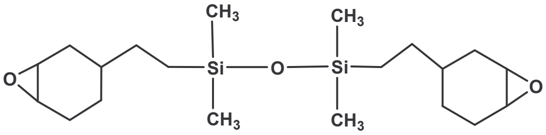
Silicone Acrylates
The silicone acrylates family is interesting for the polymerisation under UV.
The grafting of acrylate functions on the polymer organopolysiloxane is generally obtained by reaction of esterification or opening the epoxide ring with acrylates.
The free radical polymerisation process of double bonds is strongly influenced by oxygen in air and the result is that there is no cure at the surface of the coating without inertization. Another consequence is also a gradient of cure between the surface and the heart of the coating with a decrease of the solvent resistance of the top layers.
They also cause shrinkage which is prohibitive in a lot of application.

Silicone Epoxides
Bluestar Silicones has developed a large range of epoxy silicones by hydrosilylation of vinylcyclohexene oxide with a process that avoids gelling during the reaction. The monomers and polymers obtained by this process have a high purity.

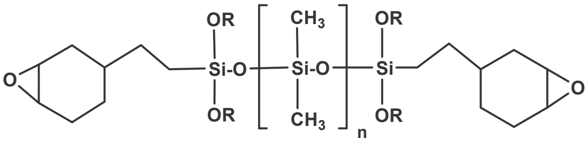
In comparison to acrylate silicones, epoxy silicones are not influenced by the oxygen in air and they have a lower shrinkage.
Many studies on such product for release applications have been done in the past. This paper is focused on one kind of structure: the end-capped functional epoxy and discusses the formulation work which has been done to improve final properties.

In the end-capped functional epoxy, two categories have been investigated:

- Silicone EPOXY 1 from Bluestar Silicones

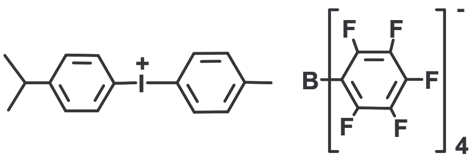


- Silicone EPOXY 2 from Bluestar Silicones



with R = H, Me, Et…

For cationic polymerisation, we have developed a photoinitiator very compatible with functional silicones: the tolylcumyliodonium tetrakis-pentafluorophenylborate commercialised under the name of Photoinitiator 2074.



This initiator is a solid with a melting point of 120-130°C. It activates the UV curing of cationic epoxy silicones. The mechanism henceforth well known is widely described. It is active as photoinitiator under UV radiation at wavelengths lower than 300nm. It is easily activated at higher wavelengths by association with a photosensitizer.

3. EXAMPLES of USE OF NANOPARTICLES in EPOXY SILICONES SYSTEMS

Cationic radiation curable silicones are used in many applications. We will discuss in the following section 3 examples where the additions of nano-particles have led to some improvement of the final properties.

3.1 Hard-Coatings

Thermoplastics, such as polycarbonate, have acquired a predominant role in numerous applications as replacement of glass. This is the case, for example, in the automotive field, where they are used for the manufacture of lenses for the headlamp units and tail light of vehicles. This is also the case in the field of spectacle trade, where they are used for the manufacturing of spectacles lenses. The main advantage of these thermoplastics is that they are lighter and less brittle than glass.
However, these materials also exhibit a major disadvantage, namely, their low hardness in comparison with that of glass. Consequently, these materials are more easily subject to scratching and to detrimental changes, even in context of normal use.
One of the solutions employed consists in producing hard-coating at the surface of the thermoplastic, in the form of transparent coating intended to improve the performance of the thermoplastic.
The main object of this work was to provide an UV curable hard-coating having scratch resistance equivalent to composition based on Thermal Hard-coating.

Material
- Thermal cure abrasion resistant coating: Flexform 40
- Silicone EPOXY 1
- Onium borate initiator : Photoinitiator PI2074 from Bluestar Silicones
- Colloidal Silica :Organosol Highlink OG502-31 from Clariant

Sample preparation
The UV Hard-Coat is prepared by mixing the siloxane resine SILICONE EPOXY 1, the photoinitator PI2074 dissolved in isopropanol alcohol and the highlink colloidal silica.
The solution of hard-coating is applied by dipping a polycarbonate plate at 20°C.
The thermal hard-coat is then dried at 25°C for 10 minutes followed by a thermal crosslinking at 122°C for ½ hour.
The UV hard-coat is allowed to drain for one minute and the system is crosslinked by passing, at the rate of 5m/min, over a UV conveyor equipped with 2 160W/cm Hg lamps. The system is dry and very hard at the outlet of the bench.

Results and Discussion
The thickness of the Flexform 40 film is two micrometers. The pencil hardness of the coating ranges from 4H to 6H. A Taber abrasion resistance test is carried out according to standard T30-015 with a load of 500g and 300 cycles with CS10F abrasive wheels. A variation in gloss of 10% is found, ie ΔHaze =10%.

The UV hard coating formulation is stable at ambient temperature and protected from the light for at least 6 months. After crosslinking, the film thickness is of 3 micrometers. The pencil Hardness is 3H immediately and greater than 4H after 24 hours. The same Taber abrasion test is used and a variation in gloss, ΔHaze =15%, is found.

3.2 Nano-composites

To date, resins based on photopolymerizable acrylates can be used to prepare for example biomedical compositions. However, these ready-to-formulate products exhibit, on use, problems of irritation and potential problems of toxicity. In addition, these products exhibit the major disadvantage of resulting in significant shrinkage in volume when they are polymerised. To overcome these disadvantages, Bluestar Silicones has already provided UV cationic silicone compositions with improved qualities, in particular as regards the very marked reduction in the phenomena of shrinkage. The main object of the present work was to provide novel biomedical compositions exhibiting, after polymerisation:
- a degree of opacity which makes possible homogeneous and simultaneous polymerisation over at least 3 millimeters in less than 1 minute.
- improved mechanical properties.

Material
- Silicone EPOXY 1
- Onium borate initiator : Photoinitiator PI2074 from Bluestar Silicones
- Colloidal Silica :Organosol Highlink OG502-31 from Clariant
- Nanopox Silica in reactive resin from Hanse Chemie

Sample Preparation
For such bulk applications, the solvent could not be evaporated just before cure, so it has to be removed prior to use in order to get good curing conditions.
Two possibilities have been tested :

- Dispersion of amorphous Silica in a Silicone phase is prepared by charging to a round bottomed flask, 15g of SILICONE EPOXY 1 stabilized by 90ppm Tinuvin 765 and 50g of silica organosol in isopropanol alcohol (Highlink OG502-31). After devolatilization of the isopropanol alcohol with stirring under reduced pressure, a dispersion of silica in the monomer SILICONE EPOXY 1 comprising 47% by weight of silica and with a particle size of less than 40nm is obtained. The solution is colourless and has a viscosity of 5000 mPa.s. In the following, this solution is referred as Silica dispersion in SILICONE EPOXY 1.
- Another possibility is to use directly commercial colloidal silica in organic reactive diluent.

Biomedical Compositions are prepared by mixing all components. The test-samples are cured for 40seconds under an UV lamp with wavelength of greater than 400nm and with a power of 600mW/cm² and tested in terms of opacity, cure depth and mechanical properties.

	A	B
Silicone EPOXY 1	52,2%	
Ground silica	47%	
Silica Dispersion in SILICONE EPOXY 1		99,2%
PI	0,8%	0,8%
ITX	70ppm	70ppm
Tinuvin 765	90ppm	90ppm

Table 1: Biomedical Composition.

Results and Discussion
The first trial compared the cure depth and the Vickers Hardness of samples A and B which have been prepared with ground silica and colloidal silica, respectively.
The composition A is a dark brown paste whereas the composition B is a clear, colourless solution.
The composition A cross-links over a thickness of less than 1 mm. The composition B cross-links over a thickness of at least 3mm and the Vickers Hardness is 40HV under a load of 500grams.
To go further, using the Nanopox colloidal silica, we have shown the impact of the increase of Nanoparticles in the composition on the mechanical properties measured by flexural strength.

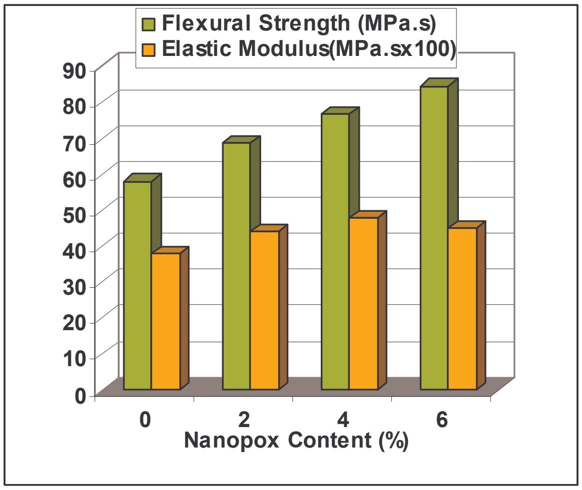


Figure 1: Flexural strength versus Nanopox Content

The impact of the colloidal silica is significant on the final mechanical properties of such composition. Futhermore, low level of nanosize fillers does not increase the opacity of the system.

3.3 Conformal Coatings

Conformal coatings are protective materials that are designed to conform to the surface of printed circuit boards for the purpose of providing a durable barrier against environmental contaminants. A conformal coating is typically applied as a thin film with a thickness of 50 to 200 micrometers.
Once again, the UV technology offers the possibility to get a very high productivity and low VOC. Furthermore,

the resin is easy to use compared to silicone acrylates since it does not require inertization with nitrogen.

Material:

- Epoxy silicone: UV CC 2000M is a silicone resin based on Silicone EPOXY 2 monomer which is ready to use without photoinitiator adduct. The resin has a viscosity comprised between 150 and 400mPa.s which enables easy filling up several millimetres and the coverage of three-dimensional objects without trapping air.
- MQ resin could be considered as precipitated silica with a size in the range from 2-3nm. Such MQ resin diluted in Silicone Epoxy are commercially available at Bluestar Silicones under the name RHODORSIL RCA251.
- Fumed silica: OX 50 from Degussa,
- Colloidal Silica: Organosol Highlink OG502-31 from Clariant,
- Nanopox Silica in reactive resin from Hanse Chemie
- POSS cubic Nanoparticles from Hydrid Plastics.

Sample preparation

6 mm thickness samples are cured by passing, at the rate of 5m/min, over a UV bench equipped with 2 160W/cm Hg lamps. The Shore A Hardness is measured after 2 hours, 24 hours and 72 hours.

100 micrometers samples on aluminium substrate are also cured and loss of weight under Taber abrasion is measured.

Results and Discussion

During a first screening, we have evaluated the compatibility of the different nanoparticles with the Silicone EPOXY 2.

The solvent based colloidal Silica Organosol has been mixed with the Silicone EPOXY 2. The solution is slightly turbid. After devolatilisation, we obtained a white high viscous paste which is not soluble in the UV CC 200M product and lead to gels formation after less than 1 hour.

10% Nanopox mixed with Silicone EPOXY 2 leads to immediate phase separation.

No further evaluations have been done with the Organosol Highlink and the Nanopox colloidal silica.

2% of POSS nanoparticles have been blend to the UV CC 2000M conformal coating. The blend is not completely homogeneous and decantation appears after 24 hours.

The RCA251 is compatible with Silicone EPOXY 2, a composition containing 30% RCA 251 (9% of MQ resin) is transparent and stable at room temperature.

The Shore A Hardness after 72 hours on the top (directly exposed to UV light) and the bottom of the samples have been measured for the compositions containing POSS and RCA251.

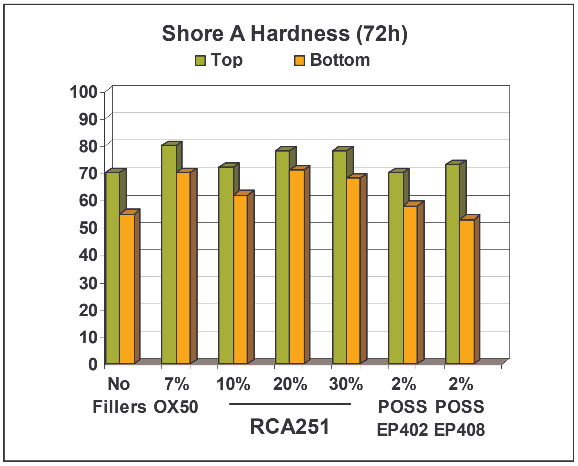


Figure 2: Shore A Hardness after 72hours.

The "No Fillers" is the composition without any fillers addition. The composition containing 7% fumed silica OX50 is the target value in terms of Hardness Shore A. However, such composition has one main disadvantage for the final application, i.e. a significant increase of the viscosity (1400mPa.s compared to the initials 250mPa.s).

The addition of 2% POSS does not improve the hardness compared to the reference without fillers. Higher content of POSS in such composition is difficult to achieve due to the poor compatibility.

The addition of 20% RCA251, which represents about 9% MQ "nano-fillers" has a significant impact on the hardness, especially on the hardness at the bottom of the sample (side not directly expose at the UV light). Furthermore, the addition of the MQ resin does not affected the viscosity (280mPa.s).

4. CONCLUSIONS

Through those three examples, we have shown that transfer of silica nanoparticles in Silicone Epoxy is not always obvious. In the case of conformal coatings application, one alternative has been found with the use of the MQ resins. Those MQ resins are completely soluble in the Silicone Epoxy and act as nano-fillers to improve the hardness of the final coating.