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# Design of bio-based self-stratified coatings targeting flame retardant applications: a systematic approach

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## Abstract

*Self-stratification is an innovative process providing a multi functional coating. The concept of self-stratifying coating is to bring the primer, intermediate and top coat properties together in a one-pot formulation. To design a self-stratifying coating, two partially incompatible resins are mixed in a solvent blend which separates spontaneously after application and curing. To compare to the traditional multi-layer coating approach, self-stratification allows reducing the number of formulation steps, chemicals used and pollution emission. However, designing a perfectly stratified coating is a challenge, taking into account the high number of parameters involved (solvents, curing temperature, viscosity, etc.). Moreover, most already designed self-stratifying coatings use oil-based epoxy resins as thermoset resin, and “greener” solutions need to be investigated. In this work, bio-based epoxy resins and silicone resins were dissolved in various solvent blends and cured under different conditions. The stratification degree and the adhesion properties on a composite substrate were investigated depending on following parameters: (i) resin properties, (ii) cross-linking epoxy rate, (iii) curing temperature and (iv) solvent evaporation rate.*

## Introduction

Usually, to design a functional coating, several layers of coatings having specific properties (e.g. adhesive, fire retardant and hydrophobic) are applied [1] (Figure 1). From an industrial point of view, these multilayered systems require complex formulation, application and curing steps, implying many constraints [2]. Self-stratification can be an alternative. Indeed, this eco-efficient process allows the formation, in only one application, of a multi functional layer film. Moreover, it allows to reduce the amount of energy, the pollution and waste generation [3][4][5]. Despite these benefits, self-stratification process is very sensitive to a wide range of parameters, such as (i) resin properties, (ii) cross-linking rate of thermoset resin and curing temperature or (iii) solvent evaporation rate.

Futhermore, the increase of stringent regulations on toxicological and environmental aspects now encourages the use of “greener” coatings. In this study, the influence of different process parameters on the self-stratification of coatings based on bio-based epoxy resins and silicon resins will be presented and fully commented.

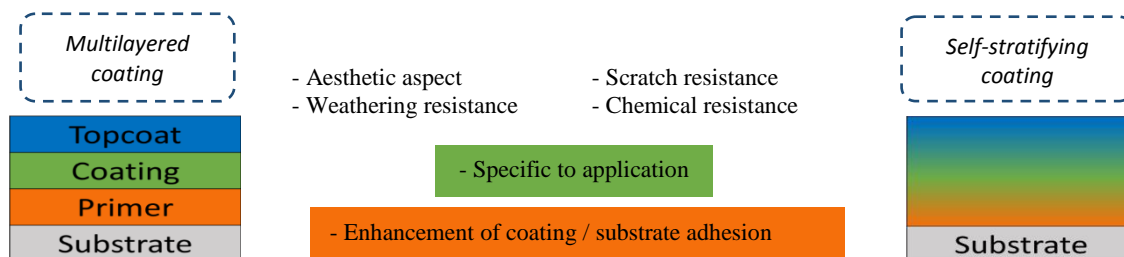


Figure 1: Self-stratifying concept

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## Experimental

### 1. Materials

To formulate self-stratifying coatings, several bio-based epoxy resins and silicone resins were selected: (i) ERISYS ISDGE (EEW: 170 g/mol, 100% solids, 40% bio content, from CVC Thermoset Specialties), Cardolite 514 SG (EEW : 417 g/mol, 100% solids, 84% bio content, from Cardolite Corporation) and a lab scale bio-based Epoxy A (reaction of isosorbide and epichlorohydrin, EEW: 176 g/mol, 100% solids, 70% bio content), (ii) Silicone S217 (phenyl silsesquioxane, 100% solids from Dow Corning), Silicone S255 (dimethyl, methyl, phenyl silicone resin, 100% solids from Dow Corning) and Silres IC678 (methoxyfunctional phenyl polysiloxane, 100% solid from Wacker). The epoxy resin was crosslinked with a polyamine (IPDA, Isophorone Diamine from Merck).

A range of commercial organic solvents was tested: Methyl isobutyl ketone (MIBK), Butylacetate (BuAc), 5-methyl-2-hexanone, Ethyl lactate, hexyl acetate, Hexyl acetate and 2-butoxyethyl acetate from Fisher Chemical.

### 2. Coating : preparation, application, curing and characterizations

To prepare the coating, each resin was dissolved separately at 30% wt/wt in a solvent blend and then mixed at a 1:1 ratio. The diamine curing agent was added to the partially incompatible system with respect of the epoxy number (1:1), and mixed for 5 minutes before the application. Coatings were applied by spraying (with an air pressure of 200 kPa) onto the composite substrate. Regular spray gun Devilbliss was used to give a wet thickness around 150-170  $\mu\text{m}$ . Following the paint application, the coating was left for 15 min at room temperature and then cured in an oven at different temperatures for 2 hours.

Coating cross sections were analyzed by Scanning Electron Microscopy with X-Ray mapping, using a JEOL JSM-7800F LV at 10 kV. Samples were polished and carbon coated before analyses.

The self-stratified systems can be classified into 4 categories depending on the stratification level: (i) Type I: perfect stratification with two well distinct layers, (ii) Type II: stratification characterized by a homogeneous concentration gradient through the film thickness, (iii) Type III: formation of isolated resin spheres (iv) Type IV: coating composed of large islands of resin. In this work, Type I or Type II patterns are targeted [6].

Cross hatch test is a quick and simple standardized method (ISO 2409 [7]) for the determination of the coating adhesion on a substrate. The level of adhesion is ranked from 0 for the best ranking to 5 for the worst.

## Results & Discussion

### 1. Influence of silicone resin properties

The choice of the resin is crucial for the stratification to occur. Properties of each thermosetting and thermoplastic resins can influence the stratification pattern of the coating. First, the two resins must be compatible to produce a “one-pot” coating in solvent blend. Following the application and the solvent evaporation, the two resins must be partially separate to obtain a stratification [1].

Formulations containing Epoxy A and one out 3 different silicone resins (Table 1) were prepared using the same solvent blend (Ethyl lactate/BuAc) and were cured 15 min at RT follow by 1h at 80°C. Coating cross sections were analyzed through microscopic analyses.

Coating with Silicone S217 (Figure 2.a) leads to Type I pattern with two distinct layers. Thanks to the chemical mapping of silicon, separation of the resins is perceptible. The silicone resin is on the top layer, and the epoxy resin sticks to the substrate. Silicone S255 combined with Epoxy A (Figure 2.b) results in Type III-IV patterns with a thin epoxy base layer. The separation between these resins are not totally achieved. Formulation with Silres IC678 (Figure 2.c) shows a well separation between layers. Interlayer adhesion failures appear between the layers, but this phenomenon is due to the sample preparation method before microscopic observations.

It can conclude that a high molecular weight of the silicon resin disturbs the stratification process, even if adhesion properties are good for all systems.

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	Silicone S217	Silicone S255	Silres IC678
Form	Solid, flakes	Solid, flakes	Liquid
MW	2500	4000	900
Stratification pattern	Type I	Type III-IV	Type I
Cross hatch test	ISO 0	ISO 0	ISO 0

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Table 1: Silicone resin properties and stratification pattern results for coatings containing Epoxy A and different silicone resins in Ethyl lactate/BuAc solvent blend.

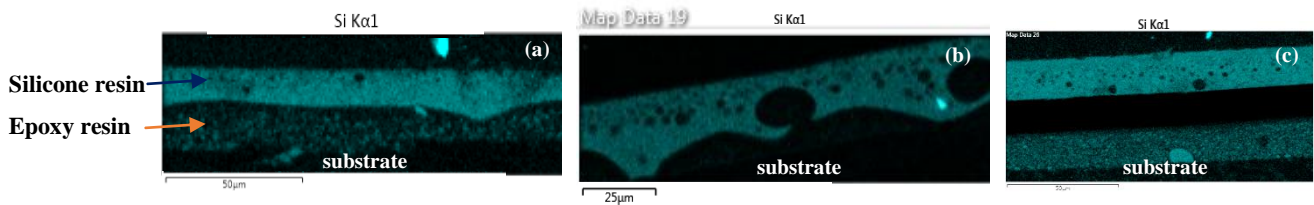


Figure 2: X-Ray mappings of Silicon for the Epoxy A/S217 (a), Epoxy A/S255 (b) and Epoxy A/IC678(c) coatings in Ethyl lactate/BuAc solvent blend

## 2. Impact of cross linking epoxy rate and curing temperature

Curing of the thermosetting resin might be a driving force for the stratification process. Indeed, during the drying step, the molecular weight of the epoxy resin increases. This phenomenon promotes the incompatibility between resins [8]. In order to explain the impact of curing temperature on the cross linking rate, DSC measurements were carried out. Cross-linking epoxy conversion is plotted versus the curing temperature and confronted with the corresponding stratification pattern of the coating (Figure 3).

At room temperature, none of the coating is stratified because the conversion rate of the epoxy resins is too low (around 10%). For the coating containing Epoxy A, when the curing temperature ranges is between 60°C and 110°C, the stratification quality is greatly improved, going respectively from type II to type I. For the system with ISDGE resin, particles rich in epoxy are dispersed in the silicone phase at 60°C. The size of these particles progressively decreases as the curing temperature increases to achieve a type I pattern at 110°C. In the case of the Cardolite containing coating, the increase of the conversion rate as a function of the curing temperature is slower than the two other epoxy resins. This is probably due to a higher MW. Thus, there is no stratification at 60°C however a type I pattern is reached at 110°C.

An increase of the curing temperature leads to an increase of the cross-linking conversion rate of the epoxy resin, thus favouring the stratification process. In fact, the cross-linking promotes the incompatibility between the epoxy and the silicone resins leading to better stratification pattern.

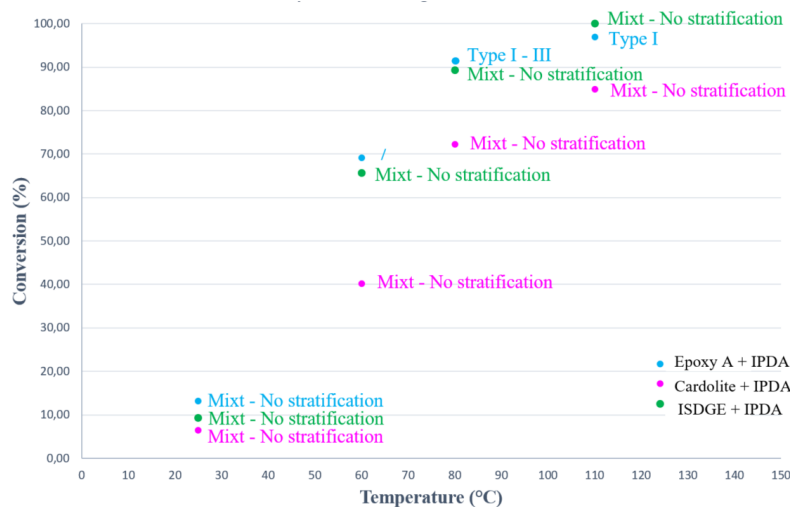


Figure 3: Impact of the curing temperature on the cross-linking conversion rate and the stratification pattern for various epoxy resins with silicone S217 coating formulations.

## 3. Influence of solvent evaporation rate

Solvent or solvent blend properties are also a crucial parameter. Each solvent can be characterized by its saturated vapour pressure (high volatility when  $T_{vap} > 50$  hPa, medium volatility  $10$  hPa  $< T_{vap} < 50$  hPa, low volatility  $T_{vap} < 10$  hPa) and its boiling point (the higher the boiling point, the lower the volatility).

To obtain a good stratification, the evaporation rate should not be too high so that the system has enough time to separated [8].

Depending on the solvent blends used (BuAc combined with another solvent, 1:1 ratio) different levels of stratification are obtained with ISDGE/Silicone S217 coatings (Table 2). X-Ray mapping of Silicon were performed to determine the stratification pattern (Figure 4).

With MIBK/BuAc and 5-methyl-2-hexanone/BuAc (Figure 4.a and 4.b), which are the most volatile blends, a perfect stratification is obtained for both coating. For Ethyl Lactate/BuAc (Figure 4.c) coating, the degree of stratification is dual: (i) Type I because a thin epoxy layer is in contact with the substrate and (ii) Type III because isolated spherical particles of epoxy are dispersed in the silicone layer. With Hexyl acetate/BuAc (Figure 4.d) solvent blend, epoxy resin is dispersed as isolated sphere particles and large islands in the silicone phase leading to Type III-IV patterns. With 2-butoxy-ethyl acetate/BuAc (Figure 4.e), the less volatile solvent blend, no stratification is observed: epoxy and silicone resins are fully mixed. Moreover, adhesion is worse with this solvent blend compared to previous coatings.

These results show that the higher the solvent evaporation rate, the better the stratification pattern. When the solvent evaporation rate is too low, the compatibility between the resins increases and the separation does not occur.

	MIBK	Butyl acetate	5-methyl-2-hexanone	Ethyl lactate	Hexyl acetate	2-butoxy ethyl acetate
Saturated vapour pressure (hPa at 20°C)	21	10.4	5.3	3	1.75	0.38
Boiling point (°C)	117	126	144	154	168	193
Stratification pattern	Type I (a)	/	Type I (b)	Type I - III (c)	Type III-IV (d)	Type III (e)
Cross hatch test	ISO 0	/	ISO 1	ISO 1	ISO 0	ISO 2

Table 2: Stratification pattern and adhesion results for the ISDGE/S217 coating prepared with different solvent blends (50:50 BuAc/other solvent).

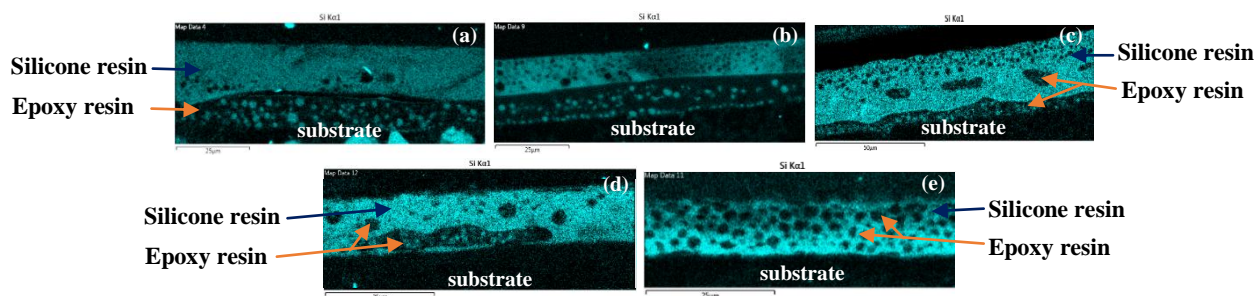


Figure 4: X-Ray mappings of Silicon for the coating with solvent blend MIBK/BuAc (a), 5-methyl-2-hexanone/BuAc (b), Ethyl lactate/BuAc (c), Hexyl acetate/BuAc (d) and 2-butoxy ethyl acetate/BuAc (e).

## Conclusion

Several self-stratified coatings containing bio based epoxy resins have been developed. The influence of epoxy and silicone properties and of the coating preparation conditions have been highlighted. In fact, if the molecular weight of the silicone resin is too high, the separation of the resins cannot occur.

Moreover, it was shown that the curing temperature and thus the cross-linking conversion rate of the epoxy resin have a significant impact on the stratification level. The higher the curing temperature, the higher the conversion rate and the better the stratification pattern.

Finally, the solvent volatility also influences the stratification process: a highly volatile solvent blend favours stratification. When the solvent is not volatile enough, the compatibility between the resins increases and no separation occurs.

This study thus shows that designing a type I self-stratifying coating is delicate and that all the above mentioned parameters must be controlled and investigated to reach the targeted structure.

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