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# Self-stratified bio-based coatings: formulation and elucidation of critical parameters governing stratification

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## Abstract

Self-stratification is an innovative one-step process used to design multi-functional coatings gathering simultaneously in a one-pot formulation the primer, the intermediate layer and the top coat properties. Many self-stratifying coatings contain oil-based epoxy resins but the literature is scarce in the development of “greener” solutions. In this work, silicone resins and bio-based epoxy resins were dissolved in various solvent blends, applied on a composite substrate and cured under different conditions to obtain stratified coatings. To reach a perfect stratification, the influence of various parameters including (i) the surface tension and the polarity of the resins, (ii) the solvents volatility, (iii) the curing temperature and (iv) the reactivity of the epoxy/amine reaction was studied by a systematic approach. In accordance with the literature, it was demonstrated that a large difference in surface energy and polarity favors resins separation. The volatility of the solvent blend was also shown to be a key factor in the stratification process. However, the predominant parameter, rarely taken into account, is the curing temperature, which impacts the cross-linking reaction of the epoxy resin. The increase in molecular weight (MW) of epoxy resins due to the cross-linking reaction favors the incompatibility between resins by increasing the difference in MW between epoxy and silicone resins. Thus, optimization of process conditions allowed the design of perfectly stratified bio-based epoxy/silicone coatings. The mechanism of film stratification was also elucidated thanks to in-situ analyses.

**Keywords**: self-stratifying coating; bio-based epoxy resin; silicone resin; surface energy; solvent volatility; cross-linking reaction

## I. Introduction

For many years, research on coatings has been constantly growing in an attempt to enhance both the process and the final properties. Conventionally, two or three distinct layers are applied one after the other: a primer coat and / or an intermediate coat to ensure good adhesion to the substrate and provide a functional property or color. A top coat is then applied to protect the lower layer from external damage and to provide a good aesthetic appearance to the coating [1]. Adhesion failures can thus be encountered at the interface between layers. Each layer requires one formulation step and one application step, followed by a specific curing step. This multilayered system thus involves many complex steps industrially demanding to meet. Consequently, an innovative and economical process has emerged: self-stratification. The purpose of such process is to form a multi-functional paint in a one-pot formulation combining primer/intermediate layer and top coat properties (Figure 1). Self-stratifying coatings are made from a blend of incompatible polymers dissolved in a solvent or solvent blend, which separate spontaneously after application and during the curing step [2][3]. In contrast to the traditional multi-layer coating approach, self-stratification reduces the number of application and drying steps, as well as the amount of chemicals used and pollutant emissions. Such coatings thus present economic and environmental advantages [4].

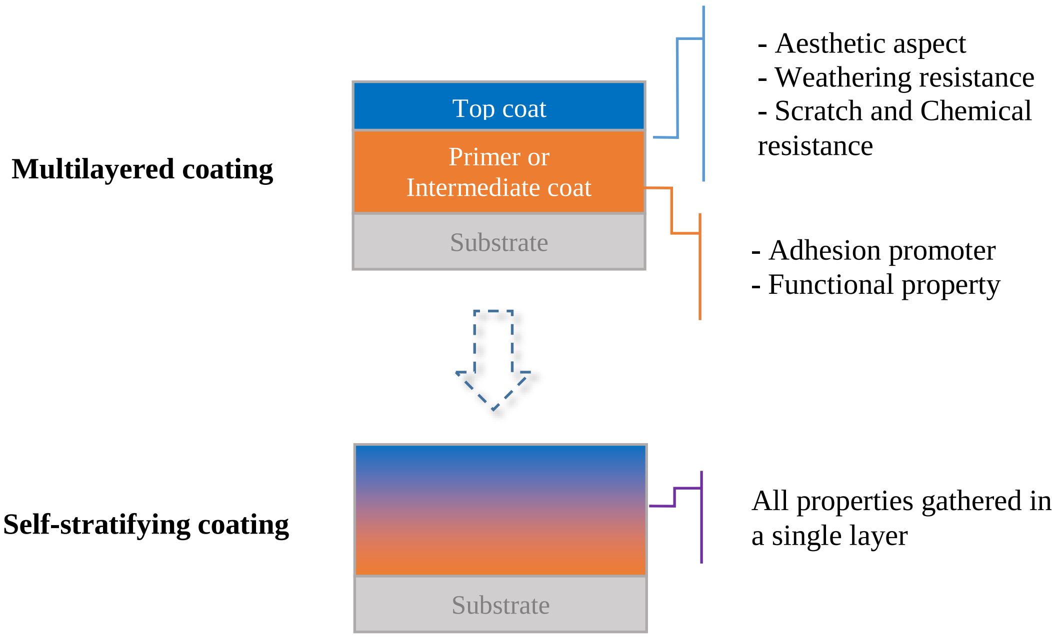


Figure 1 : Multilayered coating VS Self-stratifying coating concept

Nowadays, industrial and academic interest in self-stratifying coatings is evidenced by patents and papers reporting various types of coatings (powder [5], waterborne [6] and solventborne [7]), based on different resins, for different applications (e.g. automotive [8][9][10], self-healing [11], anti-corrosive [12] …).

A wide range of oil-based resins is available on the market to meet the needs of the coating industry: acrylic, alkyd, epoxy, polyester, polyurethane, silicone …. Nevertheless, in view of the depletion of fossil reserves and for sustainable concern, chemical industry must continue to meet society's expectations with alternative products and processes that are more respectful of human beings and their environment. Therefore, a new range of raw materials must be considered, in particular materials derived from biomass [13][14][15]. Polymers synthesized from renewable resources (e.g. vegetable oils, sugar …) could be used as binders to produce bio-based coatings. In particular, the replacement of oil-based epoxy resins, largely used in the coating industry for their interesting properties, is targeted: these resins contain Bisphenol A, an endocrine-disrupting phenolic monomer with negative impact on health and on environment. Developing bio-based alternatives to these epoxy resins by reducing their toxicity, while maintaining their properties, is becoming a priority for the industry [16]. However, the use of some of these bio-resins remains a challenge due to their (i) lack of thermal stability, (ii) ageing sensitivity, (iii) higher cost and (iv) difficulty in reaching equivalent properties with oil-based polymers. In most cases, products from renewable resources are combined by chemical reaction with appropriate petrochemical compounds to achieve the same acceptable properties [17] while obtaining a product with high bio content.

Self-stratifying coatings and bio-based resins are two different recent approaches that, if combined, could potentially lead to a technological breakthrough. Combining these concepts has thus been considered in this study through the design of self-stratifying coatings based on incompatible blends of bio-based epoxy resins and silicone resins.

In order to form the top layer of the self-stratifying systems, silicone resins are of interest because of their high incompatibility with conventional resins (such as epoxy resins) [1] and their high hydrophobicity. In addition, silicone resins are widely used for their many other interesting properties such as a high resistance to thermal degradation and weathering. To fulfil the base coat role, epoxy resins are attractive because of their high adhesion on a large variety of substrates, their high flexibility and good mechanical and chemical resistance.

However, although all conditions seem appropriate in terms of resins properties to provide a promising self-stratifying system, a large number of parameters (e.g. solvent evaporation, curing reaction, surface tension, thickness, temperature …) can influence the stratification process. Thus, formulation and development of self-stratifying coatings remains difficult to grasp and in-depth work is necessary to have a better understanding of the driving parameters for self-stratification.

Many researchers have tried to explain the self-stratification phenomenon. First of all, it should be noted that the paint application method (brush, doctor blade (or tape casting), spray, dipping) and the orientation of the painted panels (horizontally or vertically) has no influence on the stratification phenomenon [18]. In the 70's, Funke introduced the concept of blending incompatible powder polymers to produce a multifunctional self-layered coating. At first, he tried to explain this phenomenon by a difference in density between the resins, but he then asserted an influence of the viscosities and the surface energies [19][20]. Verkholantsev, in the 80's, attempted to link phase diagrams and solvent evaporation with the formation of self-stratifying coatings. Moreover, he indicated that the viscosity, the thickness of the layer and the use of a curing agent can also influence the separation [21]. In recent years, he also reported that to obtain a well self-stratified coating, specific attention must be paid to the choice of the resins and particularly to their surface tensions [11]. According to Baghdachi, stratification phenomenon should be largely kinetically controlled in common thermosetting systems [4].

In the literature, influence of some parameters of different systems are thus discussed [22] but the conclusions are sometimes contradictory according to the authors. As far as we know, no recent paper deals with a systematic approach of formulation and elucidation of critical parameters governing stratification.

Therefore, this study investigates the influence of a range of parameters on the self-stratification process of bio-based epoxy resins / silicone resin systems in order to identify the most critical ones. The first part of this paper deals with the influence of the surface tension of the resins on the stratification process. Thereafter, the influence of the solvent volatility on the stratification process is studied. Then, the impact of the curing temperature on the stratification level and of the epoxy/amine reactivity is discussed.

Moreover, to extend the available knowledge in the field of self-stratifying coatings, the in situ analysis of the stratification mechanism of one bio-based epoxy/silicone coating was performed by an innovative method of cryo-microscopy.

# II. Experimental

## 2.1. Raw materials

### 2.1.1. Epoxy resins

To formulate self-stratifying coatings, four bio-based epoxy resins were selected as thermosetting component (all are 100% solids): (i) a lab scale bio-based Epoxy A (70% bio content obtained by a reaction between isosorbide and epichlorohydrin), (ii) Erisys ISDGE (48% bio content based on isosorbide, obtained from CVC Thermoset Specialties, Moorestown, United States), (iii) Erisys GE60 (18% bio content based on sorbitol, obtained from CVC Thermoset Specialties, Moorestown, United States) and (iv) Cardolite 514 SG (84% bio content based on cashew nutshell liquid, from Cardolite Corporation, Gent, Belgium). DGEBA epoxy resin (Bisphenol-A epoxide, from Sigma Aldrich, Saint Louis, MO, USA) was used as an oil-based reference. The chemical structures and main properties of the resins are summarized in Figure 2 and Table 1.

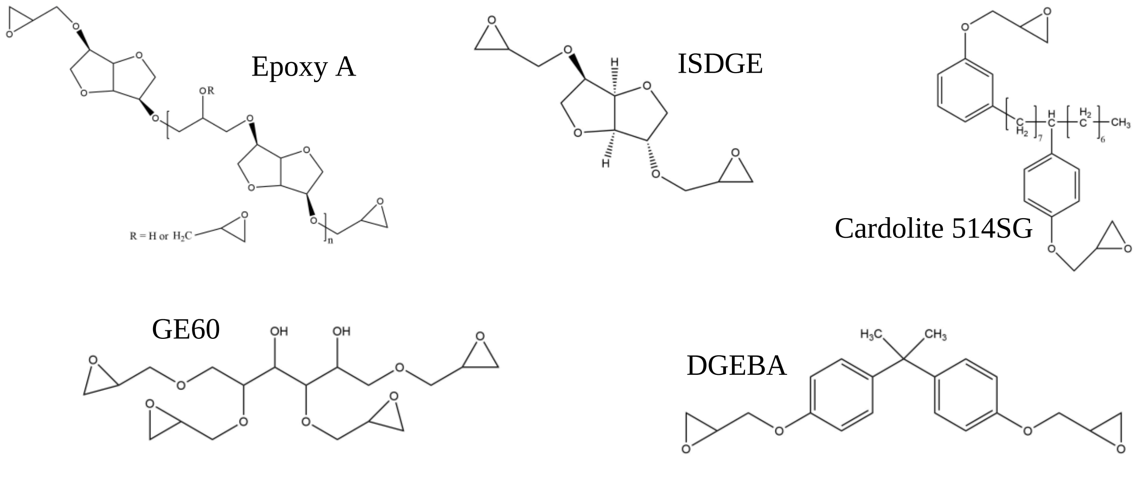


Figure 2 : Chemical structure of monomers of epoxy resin

Table 1 : Characteristics of epoxy resins

| Name | Epoxy A | Erysis GE 60 | Erysis ISDGE | CARDOLITE 514SG | DGEBA |
|---|---|---|---|---|---|
| % bio-content | 70 | 18 | 48 | 84 | 0 |
| EEW (g.eq$^{-1}$) | 176 | 160-195 | 160-180 | 417 | 176 |
| Viscosity (mPa.s) (25°C) | 7940 | 11400 | 1040 | 3620 | 9080 |
| Density (g.cm$^{-3}$) (25°C) | 1.3 | 1.27-1.30 | N/A | 1.026 | 1.16 |
| $M_n$ (g.mol$^{-1}$) (Eq. PS – THF) | 785 | 920 | 559 | 550 (52.5%)<br>1501 (47.5%) | 315 |
| Surface tension (mN.m$^{-1}$) (Wu) | 50.1 ± 3.3 | 49.9 ± 3.8 | 51.6 ± 3.5 | 36.6 ± 2.1 | 44.1 ± 2.6 |

### 2.1.2. Hardeners

To crosslink the epoxy resins in order to build a 3D network, a classical oil-based cycloaliphatic diamine (Isophorone diamine (IPDA) from Sigma-Aldrich (Saint Louis, MO, USA)) was added in stoichiometric quantity (AHEW: 42.58 g.eq$^{-1}$) (Figure 3, a).

Two bio-based curing agents from Cardolite Corporation were also tested: LITE 2002 (67% bio content, AHEW: 104 g.eq$^{-1}$) and NX 5620 (68.7% bio content, AHEW: 82 g.eq$^{-1}$) ) (Figure 3, b). These phenalkamines were obtained from Mannich reaction of cardanol.

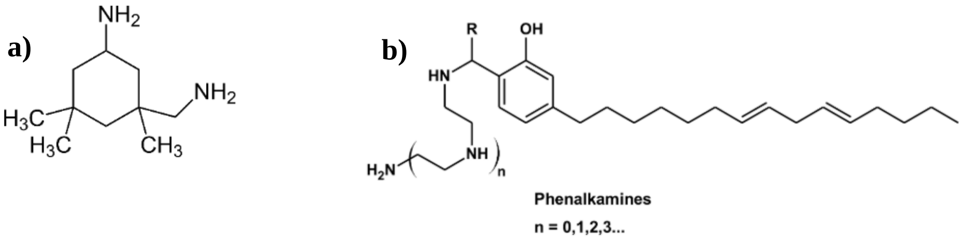


Figure 3 : Chemical structure of (a) IPDA and (b) phenalkamines

### 2.1.3. Silicone resins

In order to form the top layer of the self-stratifying systems, Silicone S217 was chosen (phenyl silsesquioxane, 100% solids from Dow Corning, Seneffe, Belgium).

### 2.1.4. Solvents

A range of commercial organic solvents were tested: Hexyl acetate, Butyl acetate and Ethyl lactate from Sigma Aldrich (Saint Louis, MO, USA), MethylIsobutylKetone, 2-butoxyethyl acetate, 5-methyl 2-hexanone from Thermo Fisher Scientific (Hampton, NH, USA). All solvents were used without any purification. Solvent properties are presented in Table 2.

Table 2 : Solvent properties

| Solvent | Surface tension (mN.m$^{-1}$) | Vapor pressure (hPa-20°C) | Boiling point (°C) | Flash point (°C) | Density (g.cm$^{-3}$) | $M_W$ (g.mol$^{-1}$) | Purity (%) |
|---|---|---|---|---|---|---|---|
| MethylIsoButyl Ketone (MIBK) | 23.5 | 21 | 117 | 14 | 0.801 | 100.16 | 99.5 |
| Butyl Acetate (BuAc) | 24.8 | 10.4 | 126 | 27 | 0.881 | 116.16 | >99.5 |
| 5-methyl 2-hexanone | 25.3 | 5.3 | 144 | 41 | 0.812 | 114.9 | 99% |
| Ethyl Lactate (EL) | 28.3 | 3 | 154 | 46 | 1.031 | 118.13 | >98% |
| Hexyl acetate | 26 | 1.75 | 172 | 56 | 0.867 | 144.21 | 99% |
| 2-butoxyethyl acetate | 28.5 | 0.49 | 192 | 76 | 0.942 | 160.21 | 98% |

### 2.1.5. Substrate

The substrate used is a composite panel made of vinyl ester resin with 30% of glass fibers provided by S3p Composites (Bretteville-sur-Laize, France). The dimensions of samples are 10 cm x 10 cm x 3 mm.

## 2.2. Coating process

Formulation, application and curing steps to produce a self-stratifying coating are described below and summarized in Figure 4.

### 2.2.1. Formulation

To make the coating, each resin (epoxy resin and silicone resin) was dissolved separately at 30 wt% in a common solvent blend. Each solution was stirred at 300 rpm with a mechanical stirrer Dispermat from Vma-Getzmann. Then, both solutions were then mixed at a 1:1 ratio with the same mechanical stirrer. The selected curing agent was added in the mixture with respect to the epoxy number (1:1). Solution was then further mixed for 5 minutes before application.

### 2.2.2. Application

Coatings were sprayed on the composite substrate at RT with an air pressure of 200 kPa in a spray booth (Labo 600 from Tricolor Industries, Décines-Charpieu, France). Regular spray gun (LG60 from Tricolor Industries) with a compact buzzard and stainless steel nozzle of 1.2 mm (suitable for low viscosity paints) was used to give a wet thickness ranging from 150 to 170 µm.

### 2.2.3. Curing

After application, the coating was left for 15 min at room temperature. Industrially, the pre-curing step at room temperature prevents the film from drying too quickly after application. Indeed, if the coating is put directly at a higher temperature a solid film form rapidly at the surface, preventing the evaporation of the solvents, leading to bubbling or blistering at the film surface during evaporation.

Moreover, at room temperature curing does not occur, or very slowly. Therefore, 15 minutes drying does not influence the separation of the resins.

Coating was then cured in an oven (C3000 oven from France Etuve, Chelles, France) for 1 hour. Different curing temperatures (60°C, 80°C, 110°C or 130°C) were tested in this study.

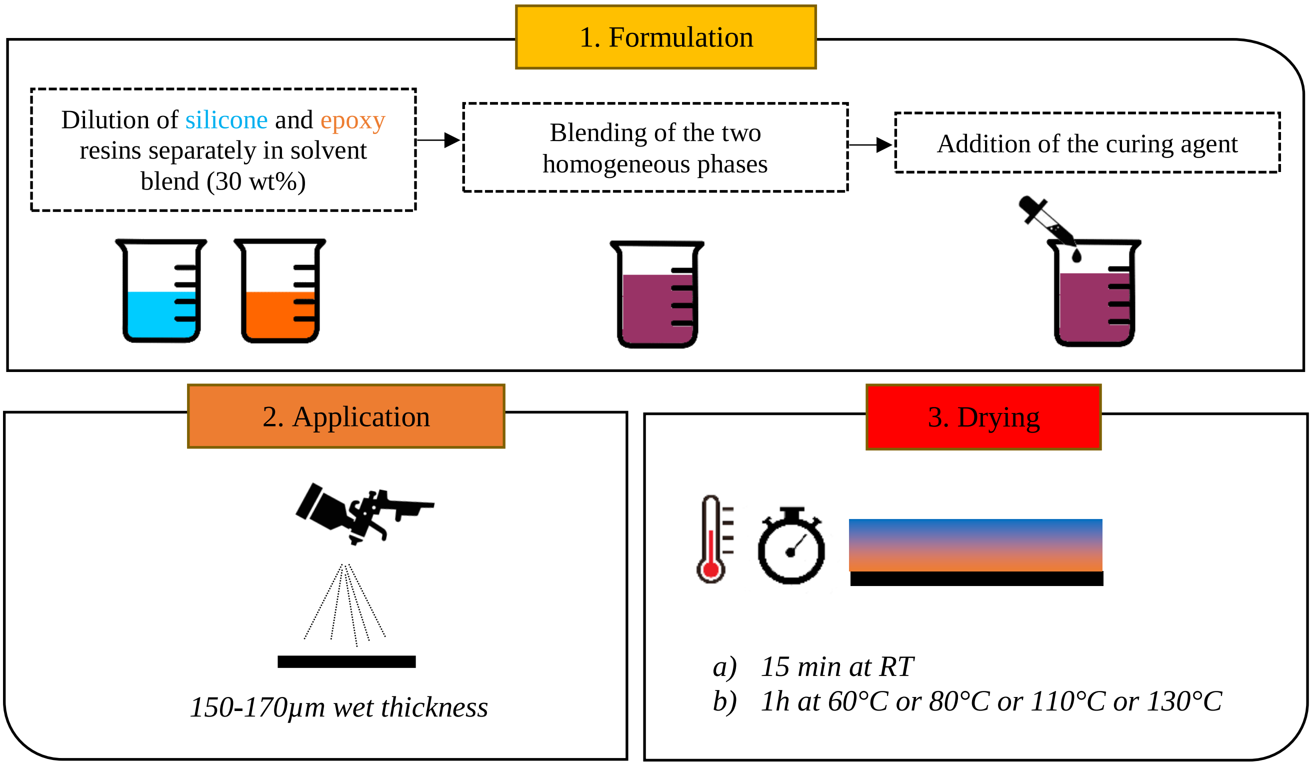


Figure 4 : Processing steps to obtain a self-stratified coating

## 2.3. Characterization techniques

### 2.3.1. Microscopic analysis to evaluate the stratification level

To determine the stratification level, coating cross sections were analyzed by Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX).

#### 2.3.1.1. Sample preparation

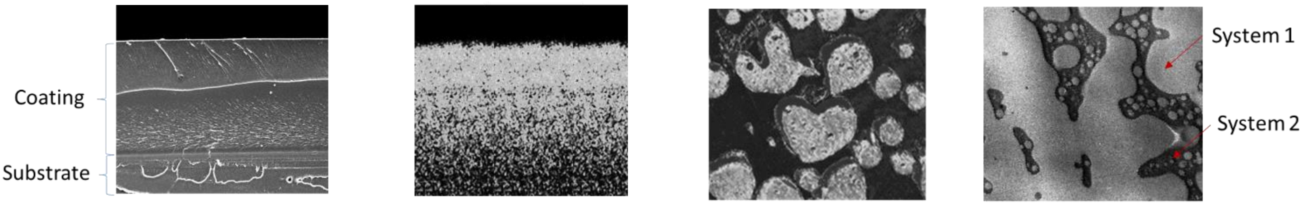
Coated composite substrates were cut with an electric saw in order to obtain 2 cm$^2$ samples. They were then put into a cylindrical mould and embedded in an epoxy resin (resin DBF 010 005 001 / hardener HY 956 010 005 002 at a 4:1 ratio (from ESCIL, Chassieu, France). Once cured for 48h at RT, the samples were polished with SiC polishing sheets (from ESCIL, France) up to the micron (grade 80 up to grade 4000) and carbon coated using a Bal-Tec SCD sputter coater to obtain clear and conductive cross-sections for microscopic observations.

#### 2.3.1.2. Scanning Electron Microscopy with X-Ray mapping (SEM-EDX)

The stratification level of each coating was characterized by Scanning Electron Microscopy with X-Ray mapping (SEM-EDX), using a JEOL JSM-7800F LV (Tokyo, Japan) at 10 kV. Mappings of Carbon, Oxygen and Silicon allow each polymer to be located throughout the coating thickness.

#### 2.3.1.3. Stratification level

The determination of coatings stratification levels are made according to the classification defined by Toussaint [18]. The ratings, ranging from Type I to Type IV (Figure 5), correspond to the following morphologies: (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 were targeted.



**Type I**
Perfect stratification

**Type II**
Homogeneous concentration gradient

**Type III**
Isolated spherical particles

**Type IV**
Large island shaped regions

Figure 5 : Type I to IV patterns defining the degree of stratification of a coating (adapted from [18])

### 2.3.2. Cryo-Scanning Electron Microscopy (cryo-SEM) to follow the stratification process

Cryo-SEM technique was adapted to study the development of the bilayer structure during the curing step. To follow the evolution of the structure once the coating applied on the substrate, each sample was dried for a specific time and directly immersed in liquid nitrogen to freeze the drying process of the coating and to fix the resins in their state into the film.

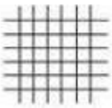
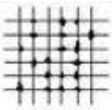
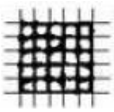
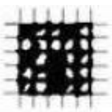
Then, samples were resized with wire cutters to obtain small cross-sections of about 5 mm x 5 mm. Using a Leica VCT100 cryo-preparation workstation and shuttle (from Leica Microsystems, Nanterre, France), samples were loaded in the sample holder (special vice) and kept frozen during their transfer in liquid nitrogen. Then, using a Leica ACE600 apparatus (high vacuum around $10^{-6}$ mbar) (from Leica Microsystems, Nanterre, France), samples were freeze-fractured at -120°C with a manual scalpel.

Finally, observations were made with a cryo-stage at -120°C in a Field Emission SEM Gemini 500 (from Zeiss, Jena, Germany) operating in high vacuum ($1.10^{-6}$ mbar in the observation chamber), at 3 kV, with a 15 or 20 µm aperture diameter, and at a working distance around 4 mm (specified more accurately on the picture). Secondary electrons were collected with the SE lens detector. Scan speed and averaging (line integrations or drift compensation mode) were adjusted during observations.

### 2.3.3. Adhesion test

The cross hatch cutter test (standard method ISO 2409 [23]) was used to determine the adhesion of the coating to the substrate. The test consists in applying and removing a pressure sensitive adhesive tape over controlled cuts made on the films. The adhesive strength of the tape lies between 6 N and 10 N per 25 mm width. For dry coating thicknesses up to 120 µm, the standard requires the cross hatch to be made of 6 cuts overlayed by another 6 perpendicular cuts, with a lateral spacing of 2 mm between the cuts. The level of adhesion is classified from 0 for the best ranking to 5 for the worst (Table 3).

Table 3 : Scoring of cross-hatch test results

| Appearance of surface of cross-cut area after tape removal |  |  |  |  |  | greater than 65% affected |
|---|---|---|---|---|---|---|
| Classification | 0 | 1 | 2 | 3 | 4 | 5 |

### 2.3.4. Surface and interfacial energy

Experimentally, surface tensions of the resins were obtained using the sessile drop method performed with a Drop Shape Analyzer (DSA100) from Krüss GmbH (Hamburg, Germany). Each epoxy resin (5 g) was respectively mixed manually with the curing agent (IPDA) in suitable proportions, applied on the polyester GF susbtrate with a tape casting to obtain a wet thickness of 50 µm, cured in a oven for 1h at 80°C and left at room temperature for at least 48h before measurement. Since the silicone resin is in flake form, the drops of solvent were deposited directly on it. Contact angles formed by different solvents at the surface of each resin were determined using the "Advance" software provided by Krüss. Three solvents with different polarities were used to calculate the surface energy: distilled water ($\gamma$ = 72.8; $\gamma^d$ = 21.8; $\gamma^p$ = 51 mN.m$^{-1}$), diiodomethane ($\gamma$ = 50.8; $\gamma^d$ = 50.8; $\gamma^p$ = 0 mN.m$^{-1}$) and formamide ($\gamma$ = 58.2; $\gamma^d$ = 39.5; $\gamma^p$ = 18.7mN.m$^{-1}$). Wu method (ASTM D 2578-67) was used to determine the total surface energy $\gamma$ as well as the dispersive $\gamma^d$ and polar $\gamma^p$ components [24]. This method is widely used for the calculation of the surface energy of polymers with low surface energy (below 40 mN.m$^{-1}$). The interfacial surface tension $\gamma_{SL}$ was determined from Equation 1:

$$\gamma_{SL} = \gamma_S + \gamma_L - \frac{4.\gamma_S^d.\gamma_L^d}{\gamma_S^d + \gamma_L^d} - \frac{4.\gamma_S^p.\gamma_L^p}{\gamma_S^p + \gamma_L^p}$$

Equation 1 : Interfacial surface tension according to Wu

with $\gamma_{SL}$: the solid-liquid interfacial surface tension, $\gamma_S$ the solid-vapour interfacial surface tension, $\gamma_L$ the liquid-vapour interfacial surface tension, $\gamma^d$: the dispersive component of the total energy and $\gamma^p$ : the polar component of the total energy.

## 2.4. Differential Scanning Calorimetry

### 2.4.1. Conversion degree

Enthalpy measurements were performed by Differential Scanning Calorimetry (DSC) using a DSC 3500 Sirius from Netzsch (Selb, Germany). Before analysis, 1 gram of epoxy resin and the corresponding weight of hardener (following the EEW) were mixed together. Part of this blend (~10mg) was introduced into an aluminum pan closed by a lid. The conversion degree $\alpha$ (%) is determined according to Equation 2:

$$\alpha = \frac{\Delta Hreact - \Delta Hpost}{\Delta Hreact} \times 100$$

Equation 2 : Conversion degree of the cross-linking reaction

with (i) $\Delta Hreact$ (J.g$^{-1}$) the total heat of curing determined by a non-isothermal scan and (ii) $\Delta Hpost$ (J.g$^{-1}$) the enthalpy of reaction after 1h of isotherm at specific temperature (corresponding to the curing temperature of the coating i.e. 60°C, 80°C, 110°C or 130°C). To determine $\Delta Hreact$, samples were heated from -40°C to 230°C at 5°C/min, then cooled to -40°C and the same temperature ramp was applied once again. This second ramp permits to ensure that cross-linking is total. $\Delta Hreact$ is determined by integration of the signal during the first ramp. $\Delta Hpost$ is determined using samples isothermally heated at specific temperature (60°C, 80°C, 110°C or 130°C) for one hour before the two successive temperature ramps (5°C/min) from -40°C to 230°C. The isothermal temperatures were reached immediately after the start of the experiment on the software. All analyses were carried out under a nitrogen flow of 50 mL/min.

### 2.4.2. Temperature of the cross-linking reaction

The temperature of maximum heat flow of epoxy/amine reaction was determined using the data obtained to determine $\Delta Hreact$. It corresponds to the temperature at the maximum of the exothermic peak.

## 2.5. Thermo-Gravimetric Analyses (TGA)

TG measurements were performed using STA 2500 Regulus from Netzsch (Selb, Germany) to quantify the solvent loss versus time at a specific temperature. The apparatus is equipped with a differential balance with a resolution of 0.03 µg. The samples are composed of 30 wt% of epoxy resin and 70 wt% of solvent blend with the addition of the crosslinking agent. Each sample (~20 mg) was put in open vitreous alumina crucibles and supported by the balance in the furnace. The nitrogen flow rate was set at 50 mL/min. The temperature program reproduced the same drying conditions as for coatings i.e. a 15 minutes isotherm at 20°C followed by a temperature rise up to a fixed temperature (80°C) at 10°C/min and a second isotherm at 80°C for 1h. Weight losses were recorded over time and then plotted.

## 2.6. Fourier Transform Infrared Spectroscopy (FTIR) – Attenuated Total Reflection (ATR)

FTIR-ATR was used to evaluate the epoxy curing reaction progress. The intensity of the peak at 915 cm$^{-1}$, corresponding to the C-O stretching vibration in the oxirane ring, allowed the determination of the conversion rate of the oxirane groups during the cross-linking reaction [25].

To reproduce the epoxy/amine crosslinking reaction, a GladiATR (PIKE Technologies, US) accessory displayed by a Waltow SD was used. It is equipped with a heating plate offering the possibility to heat the sample and therefore to record spectra according to the temperature versus time. The angle of incidence of the diamond crystal is 45 degrees and the depth of penetration of the IR beam for organic samples is about 2 microns.

Samples (epoxy resin/hardener) were placed on the ATR heated plate and infrared spectra were recorded at 80°C for 1h in a range between 400 and 4000 $cm^{-1}$ with a Fourier transform infrared spectrometer Nicolet iS50 (ThermoScientific, MA, US) in real time mode with a resolution of 4 $cm^{-1}$. The number of scans was 64.

The conversion rate (α) was calculated from the areas corresponding to the oxirane groups at around 915 $cm^{-1}$ [25]. Nevertheless, shrinkage during curing or initial sample thermostating can lead to major errors in epoxy bands integration. To avoid this difficulty, it is useful to normalize the integrated areas to a characteristic band that does not change during curing [26]. The band corresponding to the ether linkage located at 1000-1100 $cm^{-1}$ was chosen.

The conversion rate of oxirane rings is thus defined in Equation 3:

$$\alpha = 1 - \frac{\frac{A_{oxirane}(t)}{A_{oxirane}(0)}}{\frac{A_{ether}(t)}{A_{ether}(0)}}$$

Equation 3: Conversion rate of oxirane groups

with *A(0)* the initial area, and *A(t)* the area of the peak after a certain period of reaction time.

# III. Results and discussion

In this section, the influence of several parameters on the stratification level of the coatings is studied in order to design type I bio-based epoxy/silicone self-stratifying coatings: the influence of the surface tensions of the resins on the stratification process is investigated first. Thereafter, the influence of the volatility of the solvents and of the curing temperature on the cross-linking reaction and on the stratification level will be highlighted. The stratification mechanism will be detailed in the last part.

## 3.1. Influence of the surface energy

The influence of resins’ surface energy on the stratification process was investigated first. Indeed, as reported in the literature, this parameter is crucial when targeting incompatible system of polymers. Binary resins system orientation may be driven by their difference in surface energy, which can also be responsible for the system stability [20]. Indeed, Funke was the first to demonstrate that in the case of self-stratifying powder coatings, surface energy difference between two resins is the primary driving force for stratification [20] and this has been confirmed by numerous authors [22][27]. More precisely, Vink et al. who studied a range of parameters which can influence the stratification process (curing agent, particle size, solvent evaporation, solubility …) finally concluded that the surface tension of the resins has a decisive role in the formation of two distinct layers [22]. Additionally, in 2009, Kuczynska *et al.* demonstrated that, in their epoxy/acrylic formulations, the surface energy and in particular the polarity of acrylic resins are the most critical parameters for self-stratification to occur [28].

Verkholantsev reported that the selected resins must have a sufficient difference in Free Surface Energy (FSE) for separation to occur. The basis resin must be characterized by a high FSE (in order to wet spontaneously the substrate) while the stratifying resin must have a lower FSE [29]. Indeed, the stratification process is more spontaneous when the difference in surface tension between resins is large, since it avoids one phase dispersing in the other during the film formation process and since separation is promoted [30]. In this study, the basis resin chosen was an epoxy one, whether oil based or bio-based, and the stratifying resin was a silicone. Wu method was then applied to determine the surface energies of (i) the cured epoxy resins and (ii) the silicone resin (Table 4).

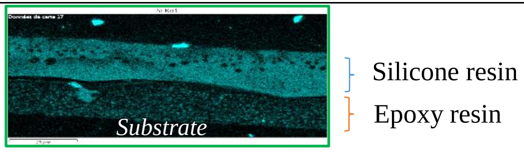
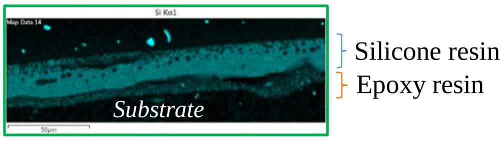
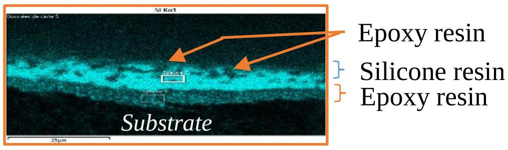
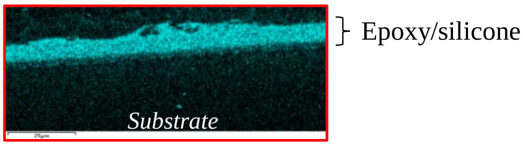
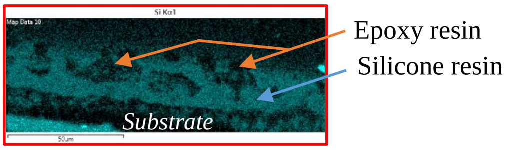
Table 4: Surface tensions of cured epoxy resins and silicone resins

| | $\gamma^d$ (mN.m$^{-1}$) | $\gamma^p$ (mN.m$^{-1}$) | $\gamma^{total}$ (mN.m$^{-1}$) |
|---|---|---|---|
| Epoxy A | 42 ± 2 | 10 ± 2 | 52 ± 4 |
| ISDGE | 41 ± 1 | 11 ± 2 | 52 ± 3 |
| GE60 | 42 ± 1 | 8 ± 3 | 50 ± 4 |
| DGEBA | 40 ± 2 | 4 ± 1 | 44 ± 3 |
| Cardolite | 37 ± 2 | 0.0 ± 0.1 | 37 ± 2 |
| Silicone S217 | 40 ± 1 | 4 ± 1 | 44 ± 2 |
| Polyester GF | 42 ± 1 | 7 ± 3 | 49 ± 4 |

Epoxy A, ISDGE and GE60 (FSEs of 52, 52 and 50 mN.m$^{-1}$, respectively) show a large difference in FSE with the silicone resin (44 mN.m$^{-1}$). Considering Verkholantsev statement, these resins are supposed to stratify more easily than DGEBA and Cardolite, possessing FSEs respectively similar (44 mN.m$^{-1}$) or lower (37 mN.m$^{-1}$) than the silicone resin.

To confirm this hypothesis, coatings based on the different epoxy resins and on the silicone resin were prepared in a 90:10 wt% Ethyl lactate/BuAc solvent blend and then cured for 1h at 80°C. The stratification level of each coating was determined by cross-section microscopic analysis and results are presented in Table 5.

Table 5: Stratification level of the different epoxy/silicone coatings in BuAc:EL (10:90) dried 1h at 80°C

| Epoxy resins | EDX Silicon mapping of the cross section | Stratification level |
|---|---|---|
| Epoxy A |  | **Type I** |
| ISDGE |  | **Type I** |
| GE60 |  | **Type I - IV** |
| DGEBA |  | **No stratification** |
| Cardolite |  | **Type IV** |

All coatings are characterized by a good adhesion to the substrate (ISO 0) and a good visual aspect (smooth and glossy) except for the coating containing Cardolite, leading to a matt film characterized by an ISO 2 adhesion.

Type I stratification is easily achieved for coatings containing Epoxy A or ISDGE resins, confirming the previous hypothesis. However, although showing a large surface energy difference with the silicone resin, GE60 stratifies with the silicone but to a lower extent than Epoxy A and ISDGE containing formulations: a Type I/Type IV mixed structure is obtained, with the presence of large epoxy islands dispersed in the silicone phase. The stratification is not complete, demonstrating that the process occurs less spontaneously than for Epoxy A and ISDGE resins. This behavior might be explained by the polar component value of epoxy resins as that of Epoxy A or ISDGE is higher than that of the silicone and of the other epoxy resins, particularly GE60. Finally, as expected, when DGEBA and Cardolite resins are used, coating stratification is much more difficult. When DGEBA resin (of similar surface tension and polarity as the silicone resin) is used, both resins remain mixed together. With the Cardolite resin, characterized by a lower surface tension than that of the silicone resin and by a polar component equal to 0, resins do not stratify. However, the location of resins can be identified: the epoxy resin is rather in the upper part of the film and the silicone resin is mainly in the lower part. The difference in surface energy and polarity therefore makes it possible to partially dissociate the two resins, but orientation of layers is reversed.

Experimental results allow demonstrating that when the difference in surface energy between the two resins is high and when the base resin has a high polarity, the stratification process is favored. This conclusion is in agreement with literature results. However, the contribution of polar part values of the resins surface energies has been highlighted for the first time to explain the self-stratification.

Although surface energy and polarity of the resins have a clear impact on the stratification, other parameters also need to be studied to get a better understanding of the stratification process. The following part focuses on the influence of the solvent properties.

## 3.2. Influence of solvent properties

Stratification of powder coating (without solvent) was demonstrated by Funke to give well-stratified coating films [20]. Then, Walbridge stated that for binary polymers blend in solution the stratification mechanism was similar and the evaporation process had no influence on the stratification [31].

Afterwards, in contrast, several authors stated that phase separation in such polymer solution was initiated by solvent evaporation [32][33][34][35]. According to these papers, it was argued that in self-stratifying systems, the first phase separation starts immediately after the application of the coating on the substrate, driven by solvent evaporation. Then the increase of incompatibility is, among other factors, due to solvent evaporation phenomenon [36].

Moreover, Vink et al. have demonstrated that to obtain a good stratification, the evaporation rate should not be too high because the binders require sufficient time to split and form a layer before the system gets too viscous [22]. Another study conducted by Verkholantsev suggested that the lower the evaporation rate and the lower the viscosity, the more spontaneous the phase separation into two distinct layers [21]. This was confirmed more recently by Beaugendre et al.: they concluded that for their oil-based epoxy/silicone coating, the evaporation rate should not be too high because the binders need enough time to form a heterogeneous structure before (i) the crosslinking reaction is complete and (ii) the system reaches a too high viscosity [37].

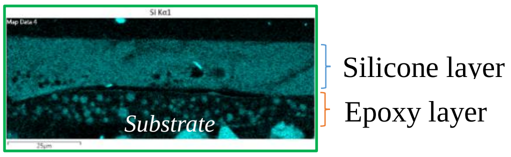
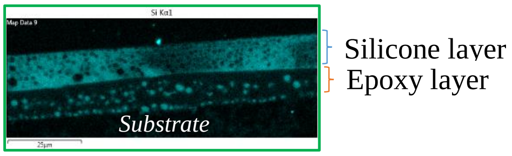
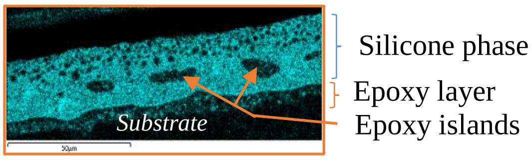
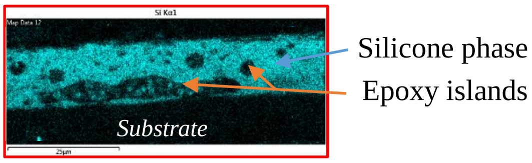
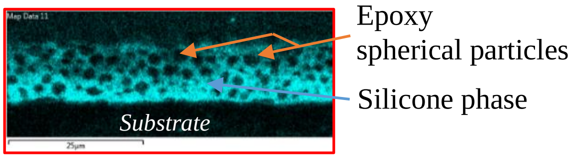
Thus, opinions about the specific influence of the solvent or solvent blend properties on the stratification process vary between authors. In this work, investigations were carried out to better understand the impact of the solvent volatility on the stratification.

Solvents can be characterized by their saturated vapor pressure (high volatility when $P_{vap} > 50$ hPa, medium volatility when 10 hPa $< P_{vap} <$ 50 hPa, low volatility when $P_{vap} < 10$ hPa) or by their boiling points (the higher the boiling point, the lower the volatility).

In the present study, solvents with $P_{vap}$ varying from 21 to 0.38 hPa were selected and mixed with Butyl Acetate (BuAc, $P_{vap}$ = 10.4 hPa at 20°C) at a 1:1 ratio. ISDGE resin was used as the base resin and the coating was dried for 15 min at RT and then cured for 1h at 80°C.

Depending on the solvent blends, different stratification levels were obtained (Table 6).

Table 6: Stratification level of ISDGE/silicone coatings prepared with different solvent blends (BuAc/other solvent at 1:1 ratio)

| Solvent combined with BuAc | Saturated vapor pressure (hPa at 20°C) | Silicon mapping of the coating cross section | Stratification level |
|---|---|---|---|
| MIBK | 21 |  | **Type I** |
| 5-methyl-2-hexanone | 5.3 |  | **Type I** |
| Ethyl lactate | 3 |  | **Type I-IV** |
| Hexyl acetate | 1.75 |  | **Type III-IV** |
| 2-butoxy ethyl acetate | 0.38 |  | **Type III** |

All the coatings were characterized by a good adhesion to the substrate (ISO 0 or ISO 1) except the coating with ISDGE in 2-butoxy ethyl acetate characterized by an ISO 2 adhesion.

With MIBK/BuAc and 5-methyl-2-hexanone/BuAc blends, which are the most volatile blends, a perfect stratification is obtained. For the coating corresponding to the Ethyl Lactate/BuAc blend, the stratification is not complete and a mixture of Type I and Type IV patterns is obtained: Type I because a thin epoxy layer is observed at the interface with the substrate and Type IV due to the presence of epoxy islands and particles into the silicone layer. When the Hexyl acetate/BuAc blend is used, epoxy resin is fully dispersed as droplets and large "islands" into the silicone phase, leading to Type III-IV stratification. Finally, with 2-butoxy-ethyl acetate/BuAc, the least volatile solvent blend, no stratification is observed as the epoxy and silicone resins are fully mixed. It is therefore obvious that the evaporation rate of the solvent has an influence on the stratification level of the coating.

In an attempt to further demonstrate the effect of solvent volatility, thermogravimetric analyses were performed on samples composed of epoxy resin (30 wt%) cured with IPDA in the previously studied solvent blends (at 70 wt%). The weight losses were recorded and are presented in Figure 6. The temperature ramp corresponds to the one used to cure the film: one isotherm is first carried out at 22°C for 15 min; then, the temperature increases up to 80°C at 10°C/min and finally a second isotherm is applied for 1 hour at 80°C.

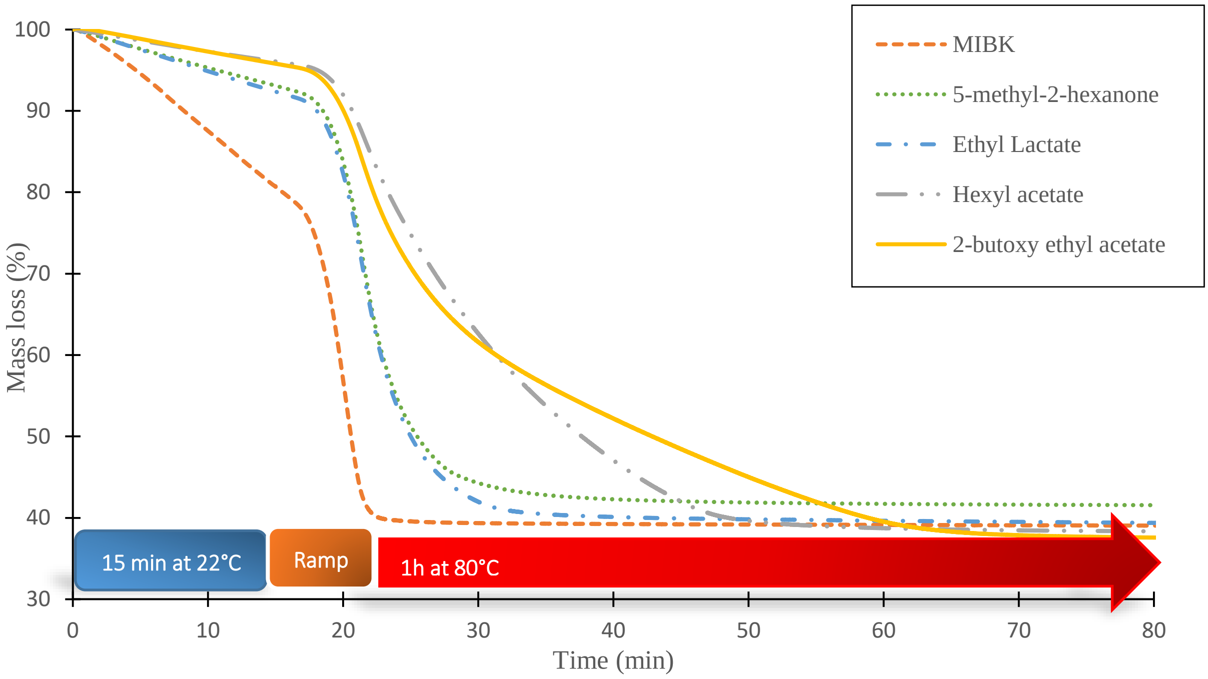


Figure 6 : Weight loss of formulations composed of ISDGE / IPDA + solvent blends (with different volatilities) exposed to similar procedure as during coating curing

First, after 24 minutes (i.e.15 min at 22°C, 6 minutes ramp to 80°C and 3 min at 80 °C), all the BuAC/MIBK solvent blend is evaporated. Blends of BuAc with 5-methyl-2-hexanone or ethyl lactate evaporate less quickly than the blend with MIBK. The solvents remain within the epoxy resin for up to 15 min at 80°C. Total evaporation is obtained after around 35 min. Finally, for the less volatile solvent blends (i.e. in the case of hexyl acetate and 2-butoxy-ethyl acetate), 54 min and 66 min are required for complete solvent evaporation, respectively. The remaining mass in the crucible only represents the epoxy with the cross-linking agent. Surprisingly, this mass is closer to 40 wt% than to the expected 30 wt%. This could be explained by the partial evaporation of the solvent blend during the manual stirring of the solution (1-2 min) and during its transfer into the TGA crucible and to the equipment. These curves confirm that blends of most volatile solvents do not remain into the film for a long time. After a maximum of 15 minutes curing at 80°C, there is no solvent left and the coatings could stratify. On the contrary, for coatings with hexyl acetate and 2-butoxy-ethyl acetate, the solvent remains into the film for a large part of the drying step (at 80°C), preventing the coatings stratification.

To conclude, these results show that stratification of the ISDGE/silicone system is favored when a medium volatile solvent blend is used, leading to a Type I stratification. In that case, resin separation takes place at the same time as solvent evaporation. The displacement of the solvent molecules drives the mobility of the resins into the film thickness. Moreover, the total crosslinking of epoxy resin may occur later, leading to the formation of stratified layers before the cross-linking reaction is complete. Coalescence of epoxy droplets could occur with the subsequent formation of a film.

On the contrary, if the solvent blend evaporates too slowly, separation between resins cannot occur. Solvents do not induce movement into the film and remain for a too long period of time in the coating film, preventing resin particles from migrating and coalescing. The epoxy resin remains solvated like the silicone one, and phase separation cannot occur before full cross-linking of the epoxy resin. Thus, when the solvent fully evaporates, the epoxy nodules remain into the silicone resin and cannot further coalesce because the 3D network formed is too rigid, hindering the stratification.

To conclude, a high solvent evaporation rate seems to be preferable for the stratification process to occur but it should not be too high because the binders need enough time to separate in a low-viscosity medium [22]. Indeed, other experiments were carried out with GE60 resin (more compatible with the solvent blends according to Hansen Solubility Parameters) and showed that with the most volatile solvent blend (BuAc/MIBK), no stratification was observed. For the GE60/silicone system, BuAc/MIBK blend evaporation rate is probably too fast to leave time for the resins to separate. Once the solvents are evaporated, the mobility of the resins is no longer ensured and the system then crosslinks, leading to a non-stratified coating.

Finally, similarly to the conclusions of Vink [22], the stratification process occurs if the solvent evaporation rate is neither too high (because the binders need enough time to separate in a low-viscosity medium) nor too low (to induce the resins displacement and to avoid the cross-linking reaction to be complete before the total evaporation of the solvents) for epoxy resins with high affinity with the solvent blend.

Solvent evaporation rate is thus a critical parameter for self-stratification to occur. However, in another study about self-stratifying coatings, Baghdachi et al. have reported that phase separation is not impacted by the evaporation rate of the solvent, but is rather largely controlled by the kinetics of crosslinking of thermoset systems [4]. Thus the cross-linking kinetics of the different epoxy resins is also studied in the following part.

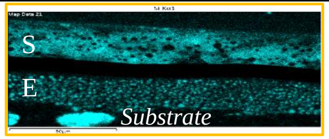
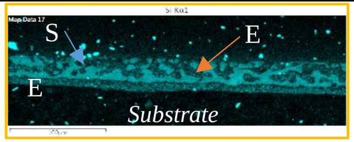
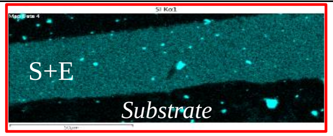
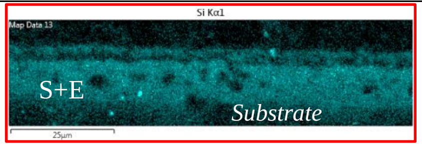
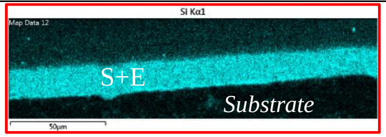
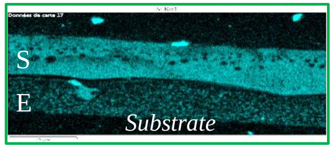
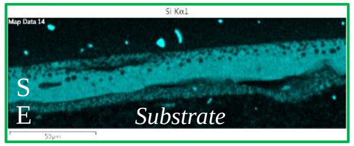
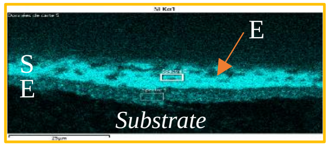
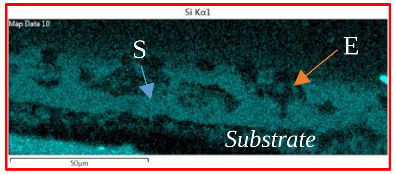
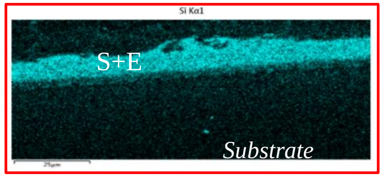
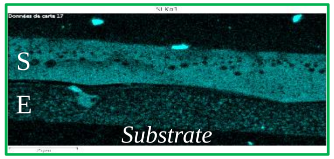
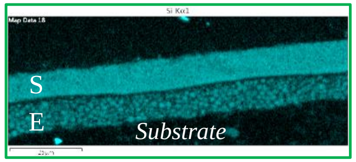
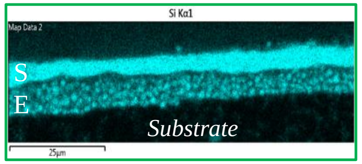
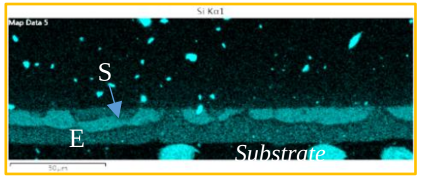
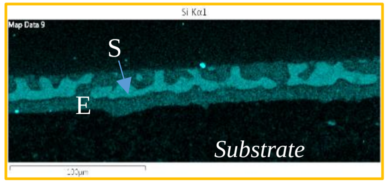
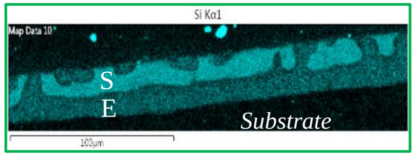
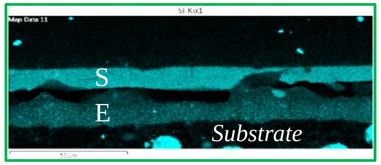
### 3.3. Influence of curing temperature

Many hypotheses have been made on the effect of the drying temperature, as it favors the crosslinking reaction and accelerates solvent evaporation. Verkholantsev assumed that heating, by increasing the solution viscosity through solvent evaporation, leads to an increase in compatibility of the resins and thereby to a decrease of phase separation [11].

However, Baghdachi concluded that if the curing step is carried out at higher temperature, the increase in molecular weight of the thermosetting resin can promote the incompatibility between resins. Nevertheless, phase separation has to take place before the full gelation of the system to give rise to two distinct layers [4].

Therefore, the curing temperature has been identified as a parameter playing a strong role on the stratification process. In order to study the impact of the curing temperature on the stratification level, coatings have been prepared using the previously described epoxy resins and curing was carried out at different temperatures (60°C, 80°C, 110°C and 130°C) for 1h. At these curing temperatures, the silicone resin is only subjected to physical drying. Cross section silicon mappings were performed to determine the stratification level (Table 7). Depending on the epoxy resin and on the curing temperature, different levels of stratification were obtained.

Table 7 : Stratification level of coatings based on epoxy and silicone resins in a 10:90 wt% BuAc/Ethyl Lactate solvent blend cured at different temperatures

| | Epoxy A | ISDGE | GE60 | CARDOLITE | DGEBA |
|---|---|---|---|---|---|
| 60°C |  <br>**Type I-III** |  <br>**Type I-IV** |  <br>**No stratification** |  <br>**No stratification** |  <br>**No stratification** |
| 80°C |  <br>**Type I** |  <br>**Type I** |  <br>**Type I-IV** |  <br>**Type IV** |  <br>**No stratification** |
| 110°C |  <br>**Type I** |  <br>**Type I** |  <br>**Type I** |  <br>**Type I-IV** |  <br>**Type I-IV** |
| 130°C | | | |  <br>**Type I** |  <br>**Type I** |

E = epoxy resin ; S = silicone resin

All the coatings were characterized by a smooth and glossy appearance with good adhesion properties (ISO 0 or 1) except for the coating made with Cardolite resin (matt film characterized by the worst adhesion (ISO 2)).

The Epoxy A containing coating, cured at 60°C, stratifies but many spherical particles of silicone resin are trapped into the epoxy base layer. At the same temperature, the coating formulated with ISDGE is heterogeneous and corresponds to a Type I or Type IV pattern depending on where the analysis is made. Large nodules of epoxy resin are indeed located into the silicone phase in the upper layer of the coating film. Moreover, a thin epoxy layer is observed at the interface between this layer and the substrate. For the coating prepared with GE60 resin at 60°C, both resins are totally mixed and no phase separation occurs.

From a curing temperature of 80°C, the coatings prepared with Epoxy A, ISDGE and GE60 stratify. However, in the case of GE60, nodules of epoxy are still observed in the top layer. At 110°C, these three coatings are perfectly stratified.

For the coatings containing DGEBA and Cardolite epoxy resins, stratification starts at higher temperature (around 110°C) compared to the other three resins. Below this temperature, epoxy and silicone resins are mixed together. At 130°C, both coatings are characterized by a Type I pattern.

These results show that the curing temperature has a crucial effect on the stratification process, which could be attributed to a modification of the crosslinking reaction of the epoxy/amine system. To confirm this hypothesis, the crosslinking kinetics has been investigated.

### 3.3.1. Study of the reactivity between epoxy resins and the curing agent according to the temperature

The curing reaction of the thermosetting resin might be a driving force for the stratification process to occur. Indeed, during the drying step, the molecular weight of the epoxy resin increases, promoting the incompatibility between epoxy and silicone resins [22].

In order to investigate the impact of the cross-linking on the coating stratification, the reaction between the different epoxy resins and the hardener (IPDA) was studied by DSC. The temperature of the exothermic peak of epoxy/amine reaction and the reaction rate were more specifically investigated.

The cross-linking reaction is characterized by a large exothermic peak on the DSC curve. Evolution of the heat flow measured by DSC for epoxy systems when the temperature increases from -40°C to 230°C at 5°C/min is shown in Figure 7.

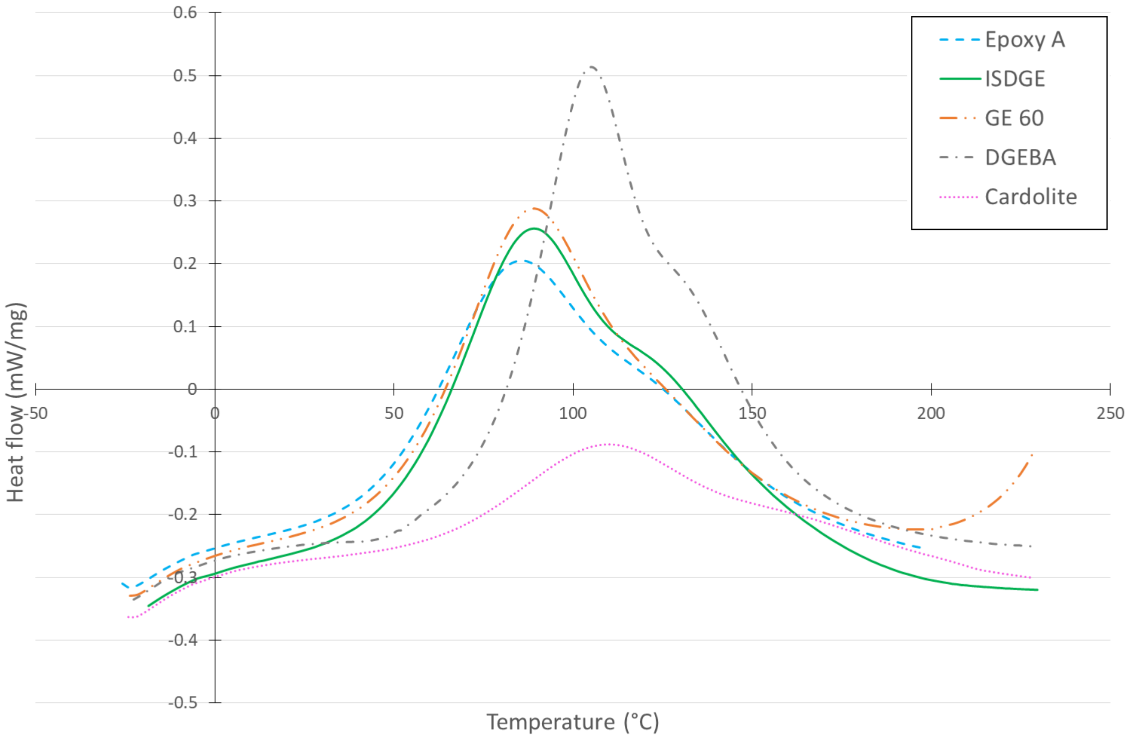


Figure 7 : DSC signal of epoxy resins reacting with IPDA (temperature rise of 5°C/min)

First of all, the temperature corresponding to the maximum heat flow provides information on the reactivity between the epoxy and the amine. The lower this temperature, the higher the reactivity of the epoxy/amine system [38]. Table 8 summarizes these temperatures and enthalpy of reaction for the different systems.

Table 8: Temperature of the maximum heat flow and enthalpy reaction measured by DSC (5°C/min) for different epoxy resins cured with IPDA

| | Epoxy A | ISDGE | GE60 | DGEBA | CARDOLITE |
|---|---|---|---|---|---|
| Temperature of maximum heat flow (°C) | 86 | 89 | 90 | 106 | 110 |
| $\Delta Hreact$ (J.g$^{-1}$) | 542 | 597 | 487 | 590 | 325 |

Those results show that the reactivity can be ranked as follows (from highly reactive to low reactive systems): Epoxy A > ISDGE > GE60 > DGEBA > Cardolite. In other words, IPDA is more reactive with Epoxy A at lower temperature (86°C) than with respectively ISDGE (89°C), GE60 (90°C), DGEBA (106°C) and Cardolite (110°C).

These temperatures correspond approximately to the temperatures at which stratification is observed in Table 7: (i) at 80°C for the coatings with Epoxy A, ISDGE and GE60 and (ii) for the coatings with DGEBA or Cardolite resins, resins separation starts at 110°C and stratification is achieved at 130°C. Therefore, to reach a Type I stratification, the coating has to be cured at a temperature similar or higher than the temperature corresponding to the maximum heat flow, at which the epoxy/hardener system shows high reactivity. Below this temperature, the reactivity of the system is not high enough to allow good separation of the resins.

Moreover, if special attention is paid to DSC signals, difference in shapes and enthalpy of reactions can be noticed. The presence of a shouldering after the main peak for DGEBA/IPDA and ISDGE/IPDA systems demonstrates that there is a large difference in reactivity between primary and secondary amines during the cross-linking reaction [38]. Exothermic peaks for the other systems do not show this difference in reactivity (no shouldering). On the other hand, the difference in shape of the Cardolite/IPDA peak compared to the other peaks is probably due to the chemical structure of the Cardolite resin, composed of long aliphatic chains. Consequently, its Epoxy Equivalent Weight (EEW) is higher (417 g/eq.) than the EEW of the other epoxy resins (around 160-180 g/eq.). It means that for an equivalent mass compared to other resins, fewer epoxy groups are available to react with amino groups, and thus the total curing heat is lower (325 J/g). The crosslinking of Cardolite resin with IPDA is less intense compared to reactions with Epoxy A, ISDGE, GE60 or DGEBA resins (~ 480 - 600 J/g).

### 3.3.2. Study of the conversion rate of the reaction between the epoxy resin and the hardener according to the temperature

Determining the temperature at which epoxy is the most reactive with the hardener is of crucial importance when designing self-stratifying coatings, as it must be correlated with the curing temperature. In order to have a better understanding of the cross-linking reaction, the conversion rates of the different epoxy resins with IPDA were determined by DSC after one-hour isotherm at the curing temperatures previously studied (60°C, 80°C, 110°C or 130°C).

Figure 8 shows the conversion rates of the different cross-linking reactions of epoxy resins as a function of curing temperatures. The corresponding stratification patterns of the formulated coatings are also mentioned in order to better visualize if a correlation between these parameters exists. The dotted vertical lines represent the temperatures of maximum heat flow determined previously (Table 8) (same color as the corresponding epoxy resin).

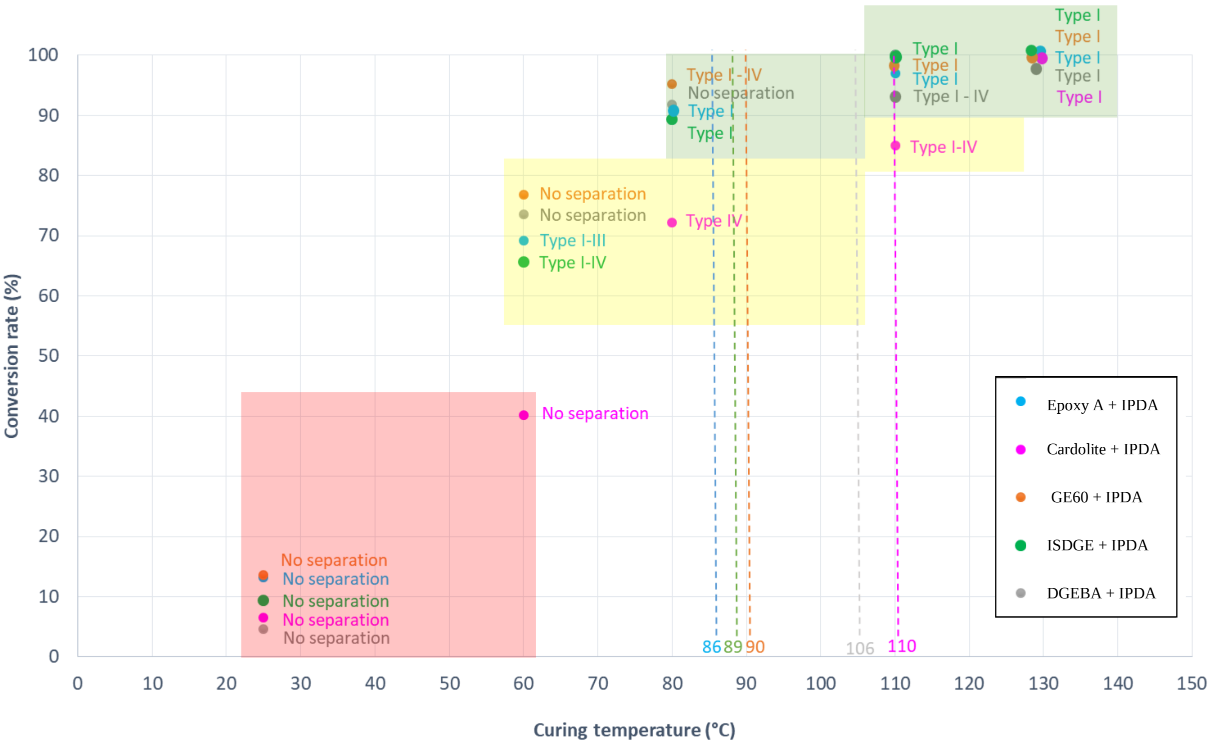


Figure 8: Conversation rate of the cross linking reaction of different epoxy resins with the hardener (IPDA) at different curing temperatures and stratification patterns obtained for the different coatings

From Figure 8, several observations can be made: (i) at room temperature (22°C), the conversion rates of all epoxy resins after 1h of curing are very low (between 5% and 10%) and none of the coatings stratifies; (ii) when the temperature increases, the conversion rates increase. Moreover, when the curing temperature is at least 10°C lower than the temperature of maximum heat flow (characteristic of the temperature at which each epoxy/hardener system is the most reactive), the conversion rates are below 85% and Type I stratification level is not obtained. Once this temperature is exceeded, high conversion rates (>90%) are achieved and a Type I stratification is observed.

Thus, the effect of the curing temperature on the stratification process is evidenced.

An increase in the cross-linking conversion rate of the epoxy resin is observed when the temperature increases. However, as reported with the DGEBA/IPDA system, a very high conversion rate does not necessarily imply a Type I stratification: at a 80°C curing temperature, although a 92% conversion rate is obtained, the resins are still mixed together. Thus, rather than the conversion rate, the temperature at which the epoxy/hardener system is the most reactive is a driving parameter to favor stratification. Below this temperature, the resin and the crosslinking agent are not reactive enough to induce resins separation; thus coatings do not self-stratify. Beyond this temperature, the epoxy cross-linking is highly reactive, favoring the incompatibility between resins and thus the stratification.

The importance of the reactivity between the epoxy resin and the hardener has thus been highlighted in this part.

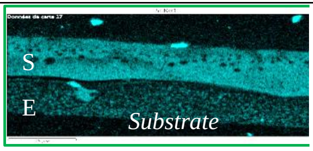
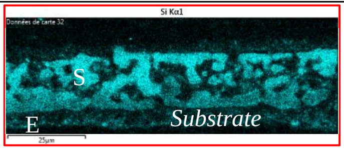
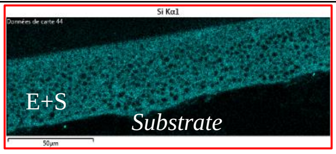
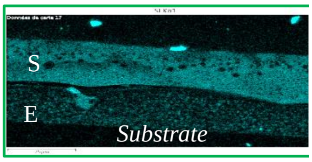
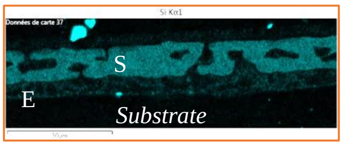
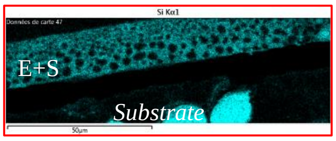
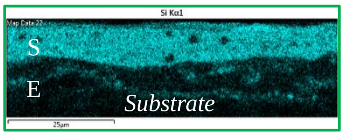
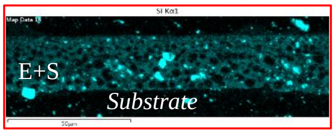
The next step concerns the study of the influence of the hardener. IPDA was substituted by bio-based hardeners to further increase the bio content of the coating formulation.

## 3.4. Influence of the hardener

The impact on the stratification level of two bio-based hardeners (LITE 2002 and NX 5620) in the Epoxy A/Silicone formulation diluted in a BuAc:EL solvent blend (10:90 wt%) was investigated.

The stratification levels obtained with LITE2002 and NX5620 were compared to those of the coatings cured with the oil-based hardener (IPDA) (Table 9). The temperatures corresponding to the maximum of the exothermic peak for each Epoxy A/hardener system with the associated reaction enthalpies are also reported in Table 9.

Table 9 : Influence of the curing agent on the stratification level of Epoxy A / silicone system

| | IPDA | LITE 2002 | NX 5620 |
|---|---|---|---|
| Viscosity (mPa.s) | 18 | 450 | 830 |
| T° of maximum heat flow (°C) | 86 | 85 | 84 |
| $\Delta Hreact$ ($J.g^{-1}$) | 542 | 298 | 378 |
| 80°C |  <br>**Type I** |  <br>**Type IV** |  <br>**Type III** |
| 110°C |  <br>**Type I** |  <br>**Type I – IV** |  <br>**Type III** |
| 130°C | / |  <br>**Type I** |  <br>**Type III** |
| Visual appearence Adhesion | Smooth, Glossy<br>ISO 0 | Smooth, Glossy<br>ISO 5 | Smooth Glossy,<br>ISO 5 |

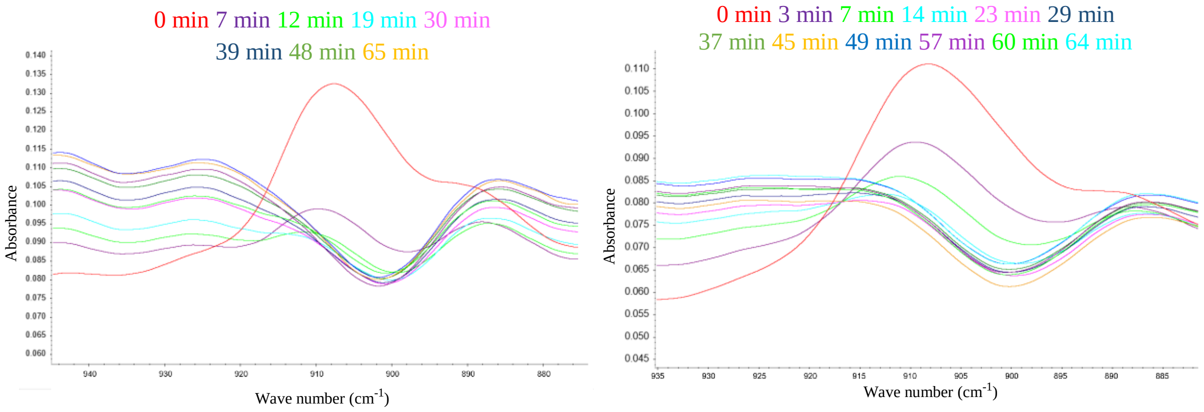
Despite similar temperatures of maximum heat flow (86°C, 85°C and 84°C), meaning in theory that the reactivity between the epoxy resin and each hardener should be similar around 80-90°C, stratification levels are not the same for all coatings. Type I stratification is obtained from 80°C for the coating with IPDA. With LITE 2002, a Type IV pattern is observed at 80°C. At 110°C, the resins orientation starts, and a well stratified system is finally obtained at 130°C. When NX 5620 curing agent is used, epoxy resin remains dispersed in the silicone phase whatever the curing temperature (80, 110 or 130°C). These differences in stratification levels should be explained by a difference in reactivity between the different epoxy resin/hardener systems, as the hardener is the only component that changes in the formulation.

First, the reaction enthalpies measured when the bio-based hardeners react with Epoxy A are lower (298 $J.g^{-1}$ and 378 $J.g^{-1}$ respectively with LITE2002 and NX5620) than when IPDA is added (542 $J.g^{-1}$). Normally, these values should be identical as the hardener has been added in the mixture in stoichiometric amount, meaning that the number of amino groups is sufficient to ensure their complete reaction with all epoxide groups.

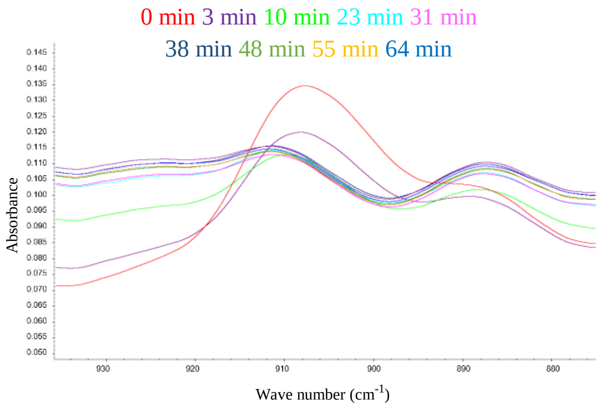
To explain the difference in reaction enthalpies, cross-linking reactions between Epoxy A resin and the various hardeners were monitored by FTIR-ATR at 80°C (because of the similar temperatures of maximum heat flow (around 80°C) for each hardener) for 1 hour. Thus, the evolution of oxirane rings content can be followed and the oxirane groups conversion rate during the cross-linking reaction can be calculated.

The comparison between the total reaction enthalpies and the conversion of oxirane rings obtained by FTIR after 1 hour at 80°C is possible because a 100% conversion rate (determined by DSC in the same temperature conditions) is obtained for both Epoxy A/LITE2002 and Epoxy A/NX5620 systems. With similar curing conditions, Epoxy A/IPDA system reaches however only 90% conversion.

At 90% conversion, ΔHreact is expected to be 487 J.g$^{-1}$ (90% of 542 J.g$^{-1}$), still higher than ΔHreact of the other two systems. Therefore, the comparison remains possible.
Zoomed views of the band centered at 909 cm$^{-1}$ corresponding to the C-O deformation of the oxirane groups during the reaction (1h at 80°C) are presented in Figure 9.



(a) IPDA (b) NX5620



(c) LITE2002

Figure 9 : FTIR spectra focus on the oxirane band showing the cross-linking reaction between Epoxy A and (a) IPDA, (b) NX5620 and (c) LITE2002 during 1h at 80°C

From the areas measured under the oxirane peaks at 909 cm$^{-1}$, the evolution of the oxirane groups conversion rate of Epoxy A versus time according to the hardener has been determined (Figure 10).

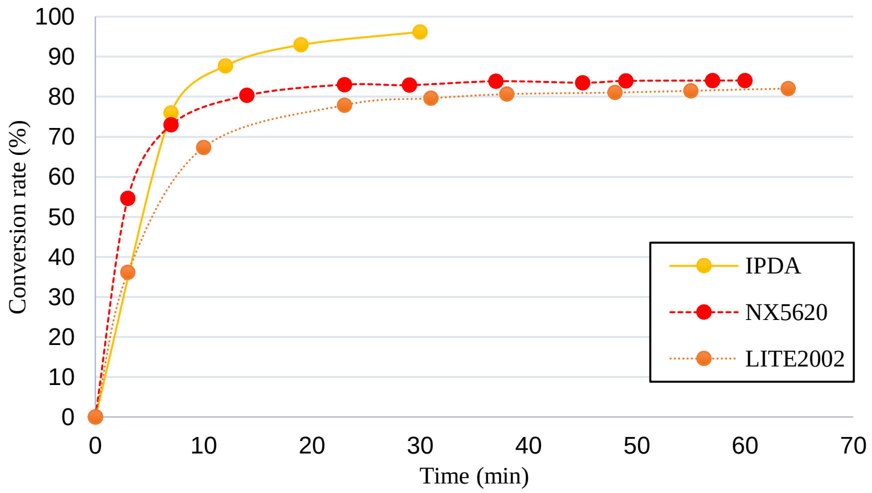


Figure 10 : Evolution of oxirane groups conversion rate of Epoxy A resin as a function of time for the different hardeners

First, it has to be mentioned that the conversion rate of oxirane groups for the Epoxy A/IPDA system has only been determined until 30 minutes : after this time, the peaks at 909 $cm^{-1}$ were not easily detectable and thus the determination of the area under the peak and hence the conversion rate was not sufficiently accurate.

All curves increase rapidly before reaching a plateau. According to the work of Gonzales et al., the abrupt increase of the oxirane groups conversion rate corresponds to the gelation step and the plateau corresponds to the diffusion controlled stage where all the primary amines are consumed [39]. From this moment, only the secondary amines can react with the oxirane groups to reach the maximal conversion rate.

The conversion rate of oxirane groups reaches 96% for the Epoxy A/IPDA system after 30 min at 80°C, meaning that almost all oxirane groups have reacted with IPDA amino groups after 1h at 80°C. It fits well with DSC measurements giving a 90% conversion rate. Conversion rates determined by FTIR are different from those determined by DSC as it is difficult to determine accurately the absorption at 909 $cm^{-1}$.

With NX5620 and LITE2002, lower epoxy conversion rates (between 80 and 85%) are obtained after 1h at 80°C, and thus the crosslinking reaction is not complete: not all oxirane groups have reacted with the amino groups of the bio-based hardeners. These results can explain the lower reaction enthalpy values previously observed for systems with LITE2002 and NX5620.

The reason why the reaction is more difficult to achieve and less complete with the bio-based hardeners can be due to their molecular structure. Indeed, phenalkamine molecules are much larger and more hindered (Figure 3) than the small IPDA molecule.

Moreover, as phenalkamines have a higher Amine Hydrogen Equivalent Weight (AHEW) compared to the cycloaliphatic amine (IPDA), a higher number of phenalkamine molecules need to be added to the mixture so that the amount of amino groups is sufficient to ensure the total reaction with all oxirane groups. Reaction is therefore impaired by steric hindrance of the molecules and of the mixture: amines have more difficulty reaching epoxy groups and opening the oxirane rings to reach the total conversion.

Thus, it has been shown that the molecular structure of the hardener has an influence on the stratification process. With a hindered hardener with less amine groups, the total conversion of the crosslinking reaction is hardly achievable and in that case, it is more difficult (as with LITE 2002) or even impossible (with NX5620) to reach a Type I stratification. The cross linking reaction is probably not enough "dynamic" to initiate a driving separation force, resulting in non-stratified films. For some systems, an increase in the curing temperature can stimulate the reaction and promote resins separation.

In addition, the difference in viscosity between the phenalkamines may also affect the activation energy of the cross-linking reaction and thus the driving force for stratification. Indeed, a system with a lower viscosity has a lower activation energy [40]. Thus, with the less viscous hardener (LITE 2002), cross-linking reaction is probably characterized by a lower activation energy than with the more viscous one (NX5620). This probably also explains why the stratification becomes possible at 130°C with LITE2002, contrary to NX 5620 hardener.

To conclude, considering systems with similar temperatures of maximum heat flow, a less viscous and more reactive hardener (i.e. a less hindered molecular structure, which implies a lower AHEW) should be more effective to obtain a stratified coating.

Moreover, coatings adhesion is strongly decreased when bio-based hardeners are used (ISO 5). Thus, IPDA remains the best alternative to cure epoxy resins and allows obtaining a stratified film with good visual aspect and adhesion properties.

Having succeeded in the development of Type I self-stratified coatings, the most promising formulations were proven to be the systems designed with Epoxy A, ISDGE or GE60 resins combined with Silicone in a BuAc:EL (10:90 %wt.) solvent blend and cured for 1h at 80°C (for Epoxy A resin) and at 110°C (for ISDGE and GE60 resins). Moreover, the influence of resins and solvent properties as well as experimental conditions on the stratification process has been highlighted. However, the stratification mechanism and more precisely the resins separation process is still obscure.

Thus, the next part of the paper focuses on the understanding of the in-situ self-stratification mechanism of the Epoxy A/silicone formulation during the curing step. This system has been selected as it requires the lowest curing temperature to achieve stratification.

### 3.5. Mechanism of stratification

In almost all literature studies, stratification is evaluated at the end of the curing step, but it is difficult to get information on the stratification process once the coating is applied on the substrate, more specifically on the kinetics of resins separation during curing. Some authors, as Abbasian et al. [41] or Langer et al. [32], have followed the resins separation in real-time using FTIR-ATR, by recording the evolution of the absorbance of specific peaks, but the resins separation process has not yet been examined microscopically. Thus, the aim of this work was also to investigate in situ the stratification mechanism of one of the bio-based epoxy/silicone coating previously obtained, showing at the end a Type I stratification. The stratification was followed by Cryo-Scanning Electron Microscopy (cryo-SEM). The coating was formulated with Epoxy A and silicone resins diluted in a BuAc:EL (10:90 wt%) solvent blend, cured for 15 min at RT followed by a 1h isotherm at 80°C.

During the pre-curing stage (15 min at RT), no cryo SEM observation could be made. No coating layer was detected at the substrate surface, probably because the non-crosslinked coating did not stick to the substrate after immersion in liquid nitrogen. Consequently, observations were made on two samples dried respectively: 15 min at RT + 10 min at 80°C and 15 min at RT + 35 min at 80°C (Figure 11).

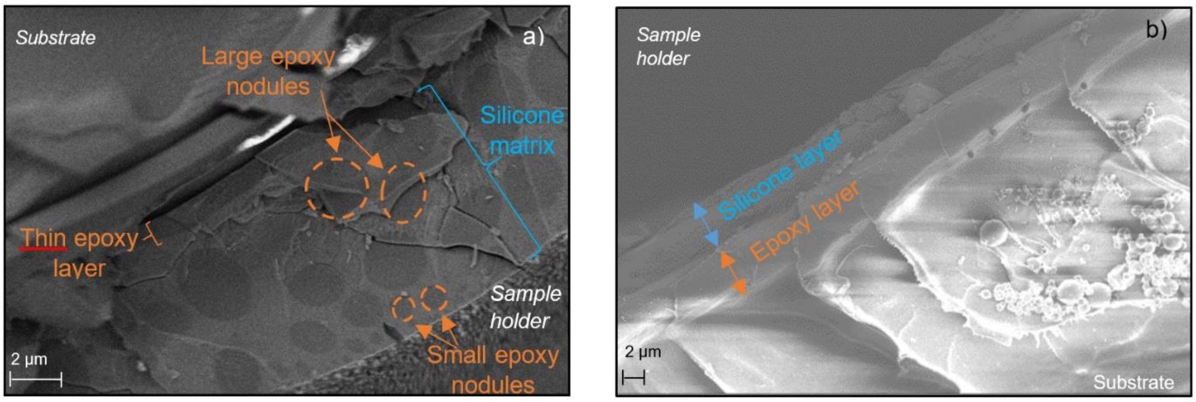


Figure 11 : Observations made by cryo-SEM of two cross-sections of Epoxy A/Silicone coatings after :
(a) 10 min at 80°C of drying (preceded by 15 min at RT) and
(b) 35 min at 80°C of drying (preceded by 15 min at RT)

After 10 min at 80°C, the film is not stratified yet: spherical particles/nodules of epoxy resin dispersed in the silicone matrix are still observable. These nodules are small at the surface and get bigger as they come closer to the substrate: they migrate through the film towards the substrate with a coalescent growth incorporating the smaller particles next to them. Once the epoxy nodules have reached the substrate, they coalesce into a single thin layer. After 35 min drying at 80°C, the film is well stratified with two distinct layers of silicone and epoxy resins.

Mechanism thus occurs as follows: the nodules composed of epoxy resin of higher surface energy migrate towards the substrate through the continuous silicone phase. Nodules grow during the migration by coalescence and form a thin layer, which sticks to the substrate and thickens as the epoxy nodules migrate. Consequently, the viscosity of the silicone resin should not increase too quickly to ensure the mobility of the epoxy nodules.

# IV. Conclusion

In this paper, several self-stratified bio-based epoxy/silicone coatings were successfully developed. The influence of resin surface tension and polarity, of solvent volatility, of the curing temperature and of the reactivity of the cross-linking reaction on the stratification process was elucidated.

It was concluded that the surface energy and polarity of the selected resins affect resins separation. Indeed, (i) a high difference in surface energies between the two resins and (ii) a base resin more polar than the stratifying resin favor their incompatibility and allow phase separation and thus stratification.
Moreover, as demonstrated in the case of epoxy/silicone coatings, the choice of the solvent blend must be adjusted. More precisely, the volatility of the solvents must be high enough to favor the resins mobility by providing enough time for the resins to coalesce and form two distinct layers before the cross-linking reaction is completed. That is not the case with a less volatile solvent blend which prevents the mobility of the resins.
The most significant fact is that the curing temperature appears to be the most critical parameter to achieve phase separation and thus self-stratification. A curing temperature similar or higher than the temperature of maximum heat flow (the temperature at which the epoxy cross-linking is the most reactive) favors resins separation and cross-linking reaction. Incompatibility between resins is promoted by an increase in the MW difference. The key role played by the curing temperature on the stratification process has been highlighted for the first time in this paper.

It was also observed that the molecular structure of the hardener may influence the stratification process. For systems with similar temperatures of maximum heat flow, a less viscous and more reactive hardener is more effective to obtain a stratified coating.

Finally, cryo-scanning electron microscopy allowed in-situ observation of self-stratification mechanism inside a coating film during the curing step, which, to our knowledge, has never been reported before.

To conclude, the design of self-stratifying coatings is a highly challenging work as these very complex systems are sensitive to many variables. Nevertheless, with this systematic study, the main influencing parameters were identified, allowing to predict whether an epoxy/silicone system will stratify or not. Selecting beforehand the most appropriate resins and optimum experimental conditions to favor the stratification process is thus now possible.

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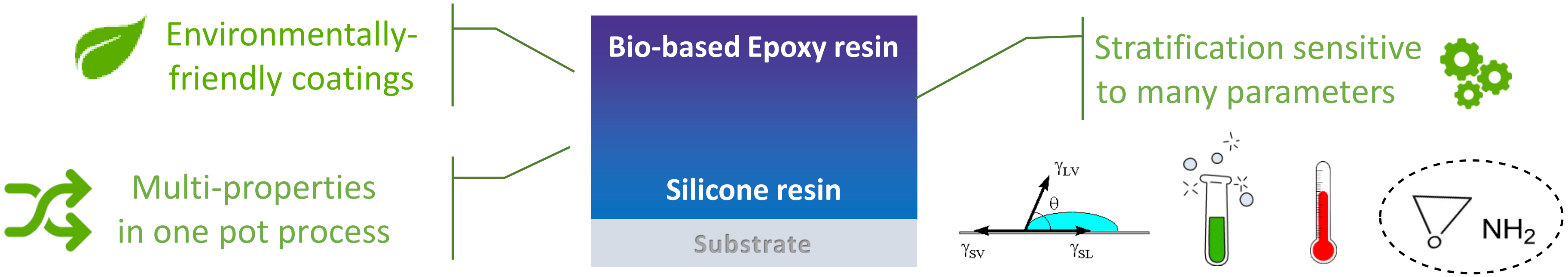
# Innovative Bio-Based Self-Stratifying Coatings



Environmentally-friendly coatings

Multi-properties in one pot process

**Bio-based Epoxy resin**

**Silicone resin**

**Substrate**

Stratification sensitive to many parameters