

Investigation of Factors Affecting Stratification Phenomenon in Epoxy-acrylic Coatings

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ABSTRACT

The stratification behaviour of different thermoplastic acrylic copolymers with one epoxy resin and its different curing agents were studied. Xylene and methyl isobutyl ketone were used as solvents of the system. Films with different thicknesses (200, 400, and 800 micron) were applied with a film applicator. Also the effect of epoxy gel time with different curing agents was tested. The results showed that coating stratification was thickness dependent, so that in higher thicknesses and the same compositions more stratified films was obtained. In addition, reduction of gel time of epoxy composition showed untraceable effect on stratification, although long duration of curing has important effect on stratification. The reaction rate of curing agent regardless of gel time is also important. According to the obtained data, it can be concluded that stratification mechanism is not diffusion dominated and it maybe convection dominated. The effect of substrates (aluminium and glass) was investigated for the coatings, and it is found that normally glass substrate yield more stratified coatings. The IR-ATR spectra showed that low surface free energy component could not be found in the bottom layer of stratified films and most of it migrated to the top surface. Our findings to some extent support the proposed theory of minimum surface free energy of the system, but the thickness dependency, reported in our paper cannot be interpreted by current theories.

Key Words:

self-stratification;
coating;
thickness effect;
epoxy;
acrylics.

INTRODUCTION

Coating systems could be composed of two or more different layers to protect substrate against corrosion and to create a good appearance regarding to decorative properties. Conventional multi-coating systems encounter some problems like poor

interfacial adhesion, high laboring costs and long duration of application. Self-stratifying coatings are attractive systems, which in the last two decades received relatively good attention [1]. These systems would be applied in a single coating instead

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of two distinct and discrete layers, so that after application a film would form with a high concentration of one resin at the air interface and a concentration gradient across the film. The presence of a concentration gradient would provide all the advantages of a dual resin system, but would eliminate the inter-coating boundary, which can be the point of failure in conventional coatings. In addition, it benefited from one-short time application. The feasibility of producing a multi-layer coating system, which can be applied in a single operation, has already been demonstrated [2-4]. In the solvent-based self-stratifying coatings, the two selected resins should have mutual incompatibility; also normally two solvents with different evaporation rates are used. Different resin pairs have been tested for obtaining self-stratifying coatings. Resin pairs such as epoxy/acrylic [5], epoxy/fluorinated resin [6] and acrylic/alkyd [7] have shown signs of stratification in different types. Regardless of practical aspects of stratified coatings, the ground or causes of stratification remain yet an interesting and arguable dilemma. There are different reasoning routes to explain this phenomenon. At first, Funke [8] tried to explain it, in regard to density differences. Later, he himself noticed the effect of the viscosity and surface free energy in self-stratification of some coating materials. One common requirement in all stratified coatings is the incompatibility of resins. Verkholtantsev [9] mainly concentrated on phase separation of the two polymers in these systems. He tried to find a relationship between phase diagrams of ingredients (two solvents plus two polymers) and the separation/stratification of the system. After him, Misev [7] with another approach but with the same concept of phase separation tried to predict the stratification. He used Hansen solubility parameters of resin pairs and solvents to predict the final situation of the coating.

They proved that immiscibility is a requirement for stratification, but not sufficient and yet some additional requirements such as suitable viscosity and surface free energy are needed to obtain stratified coatings [10].

Carr [11] concentrated on surface free energy and developed a theory to predict the stratification. According to his theory in a system containing two polymers, the following conditions need to be satisfied (Figure 1) to obtain a stratified coating:

- The system should separate into two phases dur-

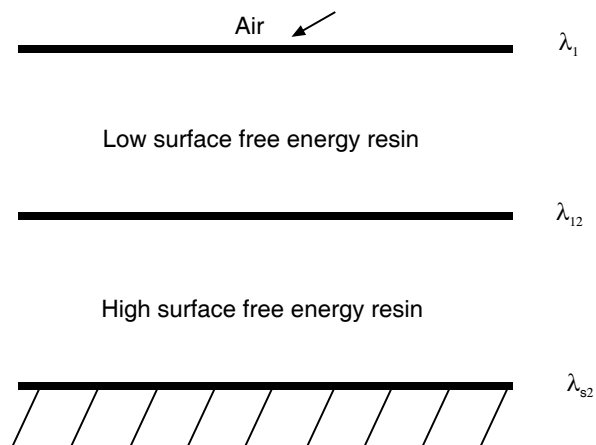


Figure 1. Schematics of self-stratified coating.

ing the drying process.

- The interfacial tension between the two liquid phases should be large enough to stop the phase being dispersed in the first phase.

- The intended base coat must spontaneously wet the substrate

- The total surface and interfacial surface free energy of the required layer sequence must be the lowest possible.

According to the above concepts the following formulas were developed, which are known as the stratification conditions:

$$\begin{aligned}\lambda_{S1} - \lambda_{S2} - \lambda_{12} &\geq 0 \\ \lambda_{S1} - \lambda_1 - \lambda_{S2} + \lambda_2 &> 0 \\ \lambda_S - \lambda_{S2} - \lambda_{12} - \lambda_1 &> 0\end{aligned}$$

In the above relations S means substrate, 1 and 2 refer to polymer components. The interfacial free energy of each pair is shown by 12, S1, S2. λ is the sign of surface free energy. Since different researchers have shown that epoxy/acrylic pairs coating systems can be stratified, in this work different grades of acrylic copolymers were selected to scrutinize the effects of film thickness, epoxy gel time and substrate on stratification. These experiments could build a base to argue better about the mechanisms responsible for stratification.

EXPERIMENTAL

Araldite GT 7071 from Vantico Company is used as epoxy resin. The epoxy resin which is used have 25%

xylene. Five different curing agents for epoxy resin were used: Aradur 830CH, Aradur 850CH, Aradur 2969CH, Aradur 43BD and 2963CH. The later two curing agents were liquid cycloaliphatic polyamines and the others were adducts of unmodified liquid polyamines. Their gel times with Araldite GY 250 (as a standard for comparison) and their viscosities and reaction rates are tabulated in Table 1.

Five different thermoplastic acrylic copolymers (Degalan' from Roehm Co.) were used, which their characteristics are shown in Table 2. The acrylic copolymers were received in powder form.

Two different substrates were used: Float glass and aluminium plates. The minor constituents of aluminium plates were: Zn: 2.06%, Pb: 0.5%, Ni: 0.58%, Fe: 1.03%, Mn: 0.57%, Cu: 0.52% and Mg: 0.29%. Aluminium plates were first cleaned with water and detergent, then soaked in methylisobutyl ketone (MiBK), and finally rinsed with acetone. For glass plates soaking in MiBK was omitted. MiBK and xylene were used as solvents. The ratio of the solvents in solvent mixture (xylene: MiBK) was 25:10. The ratio of epoxy resin+ curing agent to acrylic resin was selected as 10:5. To prepare film compositions at first epoxy and acrylic solutions with suitable amounts of solvents were mixed and stirred, and then the liquid curing agent was added. Total solid content of the mixture was adjusted on 30%. The films were applied on substrates with a film applicator. The state of the final films was evaluated by FT-IR:ATR and optical and scanning electron microscopy.

The surface free energy of epoxy resin and acrylic copolymers were measured by the sessile drop and geometric mean method. For surface free energy measurement of liquid curing agents, the Wilhelmy plate

Table 1. Specifications of curing agents.

Curing agent	Gel time (min)	Viscosity (MPa.s)	Curing speed
830CH	300	3800-5800	5
850CH	150	15000-21000	0
2969CH	90	700-900	2
43BD	45	290-450	2
2963CH	40	30-70	1

0: very fast, 5: slow

Table 2. Specifications of acrylic copolymers.

Name	Monomers*	Molecular weight (\bar{M}_w)	T _g (°C)
MB319	MMA/EA	160,000	50
AL23	BMA/MMA	160,000	50
AL25	BMA/MMA	250,000	52
P26	IBMA	180,000	66
P675	IBMA	180,000	48

*MMA: methyl methacrylate, EA: ethyl acrylate, BMA: n-butyl methacrylate, IBMA: isobutyl methacrylate

method was used.

RESULTS AND DISCUSSION

The surface free energy of all acrylic copolymers and epoxy resins (cured and raw) and curing agents were measured. The calculated solid surface free energy of solid films of used resins, through geometric mean method, can be seen in Table 3. All the acrylic copolymers have lower surface free energy in relation to the epoxy resin, so according to Carr theory [12] it is predicted that top layer should mostly comprise of acrylic copolymers. The top and bottom surfaces of the stratified coatings were studied by FTIR: ATR analysis. The ATR spectra of 7071+43BD+AL23 film were shown in

Table 3. Surface free energy of epoxies (cured and raw) and acrylics.

Material	Surface free energy (mN/m ²)
P675	28.2
AL23	31
AL25	29.9
MB319	28.6
P26	26.9
Araldite 7071	39.2
7071+ 830 CH	37.1
7071+ 850CH	36
7071+ 43BD	30.2
7071+ 2963CH	36.9
7071+ 2969CH	34.3

Figures 2 and 3. As it can be observed the specific peaks of acrylic copolymer around 1700 and 2900 on top of the film layer is very stronger in relation to the peaks of bottom layer. These results revealed that epoxy resin has moved toward substrate and acrylics are migrated to form the top layer, thus the lower layer was comprised mostly of epoxy resin. Although in both layers there were some residues of each polymer. Accordingly, in some of the well-stratified samples there were almost no sign of carbonyl groups in the bottom layer. The effect of surface free energy on stratification is significant in our tests or the results of other researchers, but despite the fact that the surface free energies of all acrylic copolymers are lower than the cured and raw epoxy resins, not all types of the acrylics are stratified, and it seems that some other parameters can attenuate the effect of surface free energy.

The surface free energies of all curing agents are around surface free energy of epoxy as tabulated in Table 4. So according to minimum surface free energy theory it can be supposed that the curing agents as an individual constituent should not migrate toward the top layer of the coating and should remain in bottom layer. Surprisingly perceptible migration of some of the curing agents to the top layer of stratified coatings was observed. This phenomenon can be easily detected by brown colour of some of the grades of hardeners, which imparted noticeable discoloration to the top layer.

This situation manifests itself more in higher thickness coatings. This phenomenon cannot be explained by minimum surface free energy theory and it makes the situation more complicated. Therefore, the general

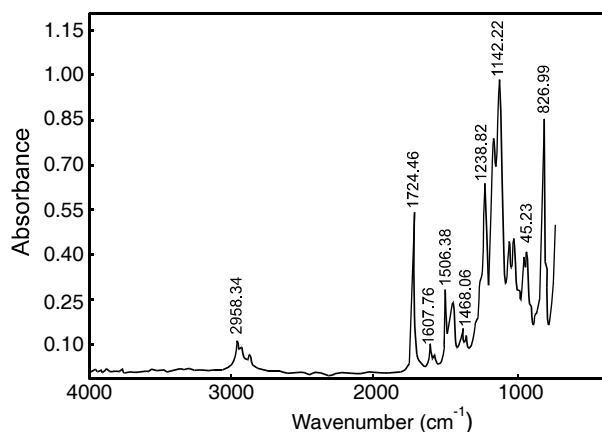


Figure 2. FTIR ATR Spectrum of epoxy acrylic mixture (7071+43BD+Al23), top of the layer.

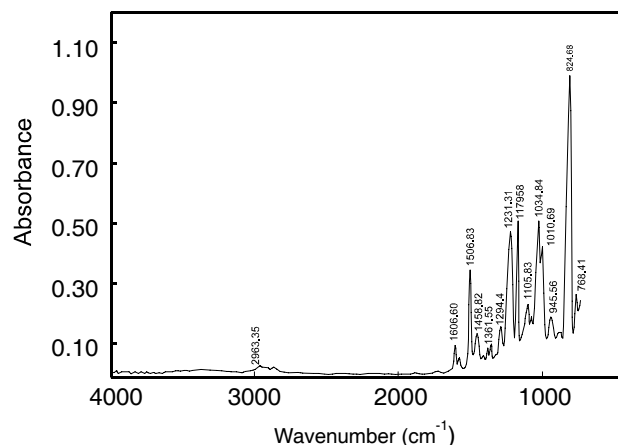


Figure 3. DFTIR ATR Spectrum of epoxy acrylic mixture (7071+43BD+Al23), bottom of the layer.

rule of minimum surface free energy does not stand perfect in all situations. This subject and the effect of the curing agent will be discussed more in later paragraphs.

Thickness and Gel Time Effect

By changing the thickness of the coatings for the same composition, it can be unveiled that whether the stratification mechanism(s) is diffusion dominated or not. By the same concept, we have tried to investigate the effect of gel time of the epoxy on stratification; so several curing agents with different gel times were used. The results are tabulated in Table 5. In the reported data, only the completely stratified coatings (not partially stratified) are considered as the stratified film.

As it can be seen in Table 5 by increasing the thickness of the film the tendency of mixture to in-layer separation (stratification) is increased. Here, in most cases stratification were observed in thicker coatings. This simply establishes that the stratification mechanism(s)

Table 4. Surface free energy of curing agent.

Curing agent	Surface free energy (mN/m ²)
830 CH	38.48
850 CH	32.93
43BD	36.56
2963CH	38.83
2969CH	47.02

are not influenced by the diffusion coefficient of stratifier (low surface free energy component). If we nominate the diffusion as a major mechanism of stratification, then it will be hard to debate why in thicker coatings more stratifications were observed. It is clear, in thicker coatings the constituents need more time to reasonably stratify themselves in layers. The other supporting data is that in thicker coatings the stratified layers are also thicker, so diffusion in general term, in no way can make such displacement and, therefore, it is

Table 5. Stratification of different curing agents and acrylic copolymers with Araldite 7071 in different thicknesses.

Mixture	Thickness (μm)		
	200	400	800
MB319 + 2969	No	No	Yes/Al, G*
MB319 + 850	No	Yes/Al	Yes/Al
MB319 + 830	No	No	No
MB319 + 2963	No	No	No
MB319 + 43BD	No	Yes/G	Yes/G
AL23 + 2969	No	No	Yes/ G
AL23 + 850	No	No	Yes/ G
AL23 + 830	No	No	No
AL23 + 2963	No	No	Yes/ G
AL23 + 43BD	No	No	Yes/ G
AL25 + 2969	No	No	Yes/ G
AL25 + 850	No	No	Yes/ G
AL25 + 830	No	No	No
AL25 + 2963	No	No	Yes/ G
AL25 + 43BD	No	No	Yes/ G
P26 + 2969	No	Yes/ G	Yes/ G
P26 + 850	No	No	Yes/ G
P26 + 830	No	No	No
P26 + 2963	No	No	Yes/ G
P26 + 43BD	No	Yes/ G	Yes/ G
P675 + 2969	No	No	No
P675 + 850	No	No	No
P675 + 830	No	No	No
P675 + 2963	No	No	No
P675 + 43BD	No	Yes/ Al	Yes/ Al

* Al: Aluminium and G: Glass.

plausible to argue that some more meaningful mechanism like a "convection type movement" shifts the components to top and bottom of the system. This suggested mechanism, in comparison to the diffusion type movement, can impart a "macro-scale displacement" in the mixture. This will be dealt with more experimental data in later publications.

Figures 4-6 show the examples of regular phase separated systems, slightly stratified coatings and strong stratified coatings, respectively. Figure 4 shows a non-stratified system on aluminium plate. As it can be seen, a regular phase separated structure is formed which is normally observed in incompatible mixtures of polymers. Figure 5 is a stratified film on glass plate that has a relatively thin stratified layer and a normal phase separated back layer. Figure 6 shows a highly stratified film, which does not show normal phase separation also in lower layer.

The other important outcome of these tests is the uncertainty about minimum surface free energy criteria. At least it can be strongly claimed that the minimum surface free energy theory cannot provide any acceptable explanation for the observed effect of the thickness.

The gel time studies showed that actually this parameter has not a significant effect on stratification within their usual time frame. Therefore, with attention to the usual gel time of these resins (Table 1) one can expect that the stratification mainly has occurred before the beginning of the gel formation. Surely, very short gel time could have prominent effect on stratification. Regardless of the effect of hardeners on gel time, the curing agents have also an interactive role in stratifica-

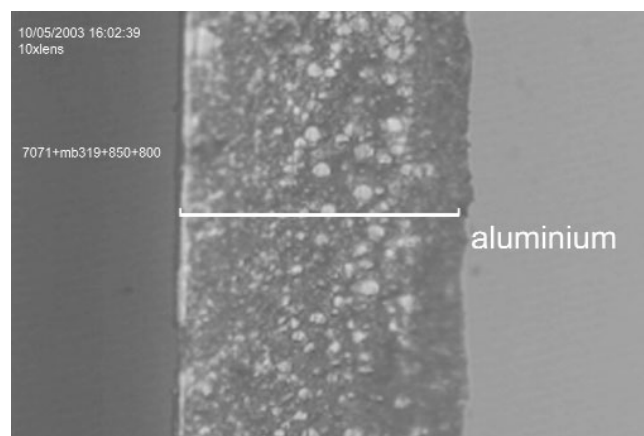


Figure 4. Example of non-stratified coating on aluminium substrate (7071+MB319+850CH, 800 micron film).

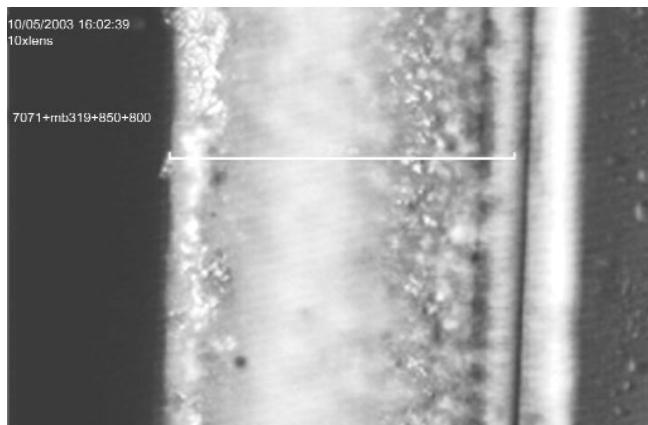


Figure 5. Example of slightly stratified coating on glass plate; picture: Right: glass; Left: stratified layer, (7071+MB319+2963, 800-micron film).

tion. In the studied compositions those which contain Aradur 830CH, have shown no sign of stratification but in the other compositions stratification was observed. Immiscibility of the cured and raw epoxy resins with thermoplastics has been studied [13] and it has been proved that the changes of chemical groups of epoxy resin and increasing of its molecular weight during curing increases the immiscibility of thermoplastic and epoxy. With regard to the above observations and discussions about the curing of epoxy resin, it can be concluded that because of long curing time of the mentioned hardener, roughly no effective increase of molecular weight of epoxy (which can assist the phase separation) have occurred during the time frame that stratified layer may develop. As other researchers stated normally cloudy solution or nonhomogeneous mix-

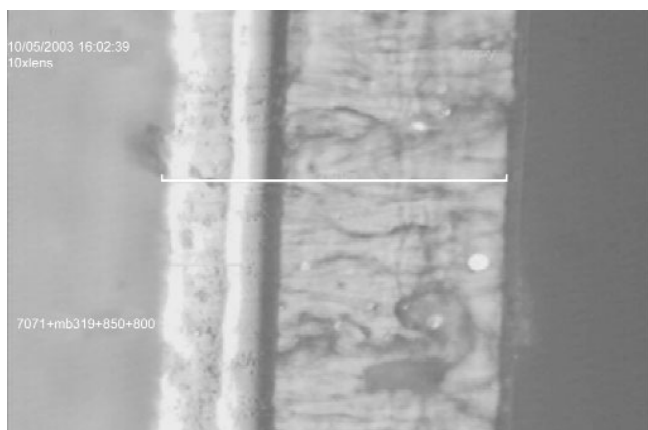


Figure 6. Strong stratified coating on glass plates; picture: Right: glass; Left: stratified layer (7071+AL23+ 2969CH, 800-micron film)

tures lead to better stratified layers [14], which was also observed in our experiments. In evaluating the stratification behaviour of the films with different curing agents, if we consider this fact that in some cases, the curing agent partially migrated to the top layer of stratified film; it is plausible to assume that in addition to curing, the chemical structure of the curing agent affects the phase separation or compatibility of phases in the liquid mixture before stratification. Therefore, the role of curing agents should not only be interpreted as the hardener of the epoxy, but also it should be seen as the fifth component of the system, that could affect the phase separation or compatibility of the system.

Substrate Effect

The stratification of declared coating compositions were tested on two kinds of substrates: aluminium and glass. As it can be observed in Table 5, that most of the stratified coatings are formed on glass substrates. According to Carr theory [11], the ability of one of the resin components to selective wetting of the substrate is a requirement for obtaining stratified coatings. In other word, the interfacial tension between one of the mixture components and the substrate should be very low, and one of the resin components should have a selective affinity for the substrate. From the viewpoint of the substrate surface free energy, both of aluminium and soda-lime glass have high surface free energy (about 660 and 330 mN/m², respectively in clean environment), thus it can be concluded that both resins are able to wet the substrate easily, and from this viewpoint one cannot make a distinct difference between them. Though epoxy resin may have more affinity to both substrates compared to acrylic copolymers, but the results are not compatible with the accepted preliminary theory. Therefore, we think that, although the minimum surface free energy of the system plays a non-negligible role on the stratification, but the conditions of substrate wetting in the mentioned theory does not coincide well with the reality of the observations made in this work and some other works [5,16]. It is worthy to note that in adsorption studies, in addition to chemical affinity of the components to the solid surface, the entropy reduction of the polymeric chains are also important, even so that entropic energies may become more important than enthalpic energies for adsorption [15]. If the large difference between the molecular

weight of the two polymeric components is considered, as it works in favour of strengthening the entropic effects, it can be argued that why in most cases a pure layer of epoxy resin in the base layer was not achieved (Figures 2-5).

From another viewpoint it is also interesting to hint that the substrate attraction does not have a long-range effect that can be effective through several microns. We have checked the surface free energy changes of epoxy resin on high free energy surfaces, and it was shown that this effect can only be observed until a maximum of about 18 nm, and after that it is completely screened out and there would not be any sign of substrate [17].

For the time being there exists no other suitable explanations for substrate effect, unless detailed studies on the competition between enthalpic and entropic effects on adsorption are carried out.

We think that the minimum surface free energy theory cannot simply be extended from thin films to thick films and in doing so it will suffer from some important shortcomings and their proofs in thin films (less than about 2 microns) are more reasonable.

CONCLUSION

It was shown that self-stratification is thickness dependent. In addition, it is observed that reduction of the gel time of epoxy resin has no effect on the stratification behaviour. In our samples when the gel time was too long, so most of the solvents were evaporated and no stratification was observed. Although obtained data showed that curing of epoxy resin, before the gel point has a decisive role in self-stratification, but curing, which increases the molecular weight of epoxy chains, it also increases the incompatibility between the phases as well. Despite of high surface free energy of the curing agents, they had been migrated to the top layer of the stratified coatings. It seems that curing agents, also as a chemical independent entity, affect the system, so that they influence on liquid-liquid phase separation before gelation of the system and migrate to the top layer of the film.

According to the data, it can be concluded that self-stratification mechanism is not diffusion-dominated. It may be a convection-dominated mechanism.

Regarding to the substrate effect, it was observed

that despite of higher surface free energy of aluminium normally, coating on glass substrates showed more stratification.

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