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Experimental and modelling study of the radiative curing of a polyester-based coating

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Abstract

This experimental investigation is structured to describe the thermal behaviour of a polyester+TGIC powder coating during infrared curing. The study hence correlates thermal modelling of the cure process and kinetics studies. First, the curing kinetics is determined using DSC experiments and modelling with the software Matlab. The results from this study are then used to study the infrared curing efficiency. Medium wave infrared leads to the fastest cure. Moreover, coupling the thermal modelling of the cure process and the kinetics has enabled us to develop a model predicting the evolution of the temperature and the degree of conversion, using the hypothesis that the paint film and the substrate are at the same temperature.

Keywords: Thermosets; Powder coatings; Kinetics; Differential scanning calorimetry; Infrared radiation; Curing; Thermal transfer

1. Introduction

Powder coatings are used by a great variety of industries such as those manufacturing automobiles, household appliances (radiators, control/switch boxes, metal furniture, windows) .... Due to the VOC regulations, the trend is definitely away from organic solvent based systems in coating techniques, and powder coatings are well positioned in the market since several years. These powders are fully solid paints which can be melted on various supports (metal, wood, ceramics, plastics ...) to form a continuous layer.

The first thermosetting coatings appeared in 1955–1960. The European Council of the Paint, Printing Ink and Artists' Colours Industry (CEPE) [1] indicates that powder coatings represented 5% of the market value and 7% of the production volume in 2001. This was equivalent to more than 400 000 tons produced with 35 000 tons in France and 110 000 tons in Italy.

Powder coatings present numerous advantages [2]. Some of them are listed below:

(1) Powder coatings are free of VOC and therefore induce very little pollution.
(2) They reduce drastically industrial rejections as the non-deposited powder can be recovered and recycled.
(3) They are non-flammable, and consequently allow better working conditions.
(4) The application of the powder does not require a high precision and it is no more necessary to check the viscosity of the paint mixture or to mix solvents.
(5) They are economically attractive as a single application is generally sufficient.
(6) The use of powder coatings eliminates the problem generally associated with solvent-based paints: bubble and crack formation during the solvent elimination. The coating finish is more uniform and more resistant to mechanical impact.

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Nomenclature

Cp	heat capacity	$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
e	thickness	m
E	activation energy	$\text{J}\cdot\text{mole}^{-1}$
h	convective exchange coefficient	$\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$
ΔH_0	total specific heat of the polymerisation reaction	$\text{J}\cdot\text{kg}^{-1}$
ΔH_t	partial specific heat of the polymerisation reaction at the time t	$\text{J}\cdot\text{kg}^{-1}$
k	Arrhenius parameter	s^{-1}
k_0	pre-exponential factor	s^{-1}
m, n	order of reaction	
Q_0	incident radiative flux	$\text{W}\cdot\text{m}^{-2}$
Q_1	energy reflected by the paint film	$\text{W}\cdot\text{m}^{-2}$
Q_2	energy absorbed by the paint film	$\text{W}\cdot\text{m}^{-2}$
Q_3	energy reflected by the substrate and transmitted by the paint	$\text{W}\cdot\text{m}^{-2}$
Q_4	energy absorbed by the paint film	$\text{W}\cdot\text{m}^{-2}$
Q_5	energy absorbed by the metallic substrate	$\text{W}\cdot\text{m}^{-2}$
R	universal gas constant	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
T	temperature	K
T_1	temperature of the wall under the sample	K
T_2	temperature of the wall upper the sample	K
Tg	glass transition temperature	K
x	degree of conversion	

Greek symbols

α	absorption coefficient	
ε	emissivity	
ρ^*	reflection coefficient	
ρ	volumic mass	$\text{kg}\cdot\text{m}^{-3}$
τ	transmission coefficient	
σ	Stefan–Boltzmann constant	$\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-4}$

Subscripts

p	paint film
sup	metallic substrate
ai	under the substrate
as	on top of the paint

In spite of these advantages, powder coatings have not found yet the success they deserve and their main application domains remain unchanged: furniture, domestic appliances, heaters, car accessories. The main limitations are their high melting points and the difficult use on non-metallic support. Nevertheless, large leading car companies are investigating the possibility of using powder painting (PSA, BMW).

Cure kinetics studies of thermosetting powder coatings have been widely described in the literature [9–15]. Nonetheless, few papers correlate thermal modelling of the cure process and kinetics studies. In order to build the basis for a better control of the curing process, the present study aims to describe the thermal behaviour of powder coatings during curing.

This paper hence describes the study of the curing process of a thermoset powder coating of the polyester/triglycidylisocyanurate (TGIC) type. The curing behaviour of this powder and especially its cure kinetics have been studied by differential scanning calorimetry (DSC), while the heat transfer has been studied by employing three kinds of infrared sources to cure this powder. Coupled thermal and kinetic models have finally been established to predict the degree of conversion and the temperature of the film.

2. Theoretical background

Powder coatings are finely ground plastic particles consisting of resin, crosslinker in thermoset powders, pigments & extenders, and various flow additives and fillers to achieve specific properties. They are principally based on epoxy, polyester, hybrid (combinations of acid polyester and epoxy) resins and polyurethane resins. Generally they are either thermosetting or thermoplastics coatings, but quite recently UV-curable coatings (the reaction is initiated by UV radiation) [3] and low-temperature coatings designed for heat sensitive substrates [4] have appeared on the coatings market.

There are few recent publications on powder coatings, describing the great potential of powder coating techniques and the strong secrecy maintained by powder coatings' manufacturers. In 1998, Misev et al. [2] presented a synthesis of the powder coating techniques and the new possible developments of these techniques. Among the different publications, one can find articles focusing on the powder formulation [5], the application of the powder [6,7] or the cure characterisation [8].

There are different ways to characterise the cure of powder coatings; some of them are presented in the following.

2.1. Curing kinetics

Cure kinetics have become an important tool for thermoset characterisation and there is an extensive body of literature describing the use of DSC (differential scanning calorimetry) to investigate reaction kinetics [8,10,12]. Some of these publications correlate the cure kinetics study with the study of the rheological behaviour of the powder coatings during curing, as it is expected to obtain a better understanding of the relationships between the thermal and rheological behaviour and the surface build-up during curing [8].

DSC measures the heat flow of the reaction process in isothermal or dynamical (constant heating rate) experiments and it is generally assumed that at any given time or temperature the rate of exchanged heat is proportional to the overall conversion rate $\mathrm{d}x/\mathrm{d}t$ [8]. Different models that describe the cure kinetics of thermosets exist. For example, it is well known that the cure reaction is autocatalysed in epoxy systems and the autocatalytic model is [8]:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \left(k_2 + k_1 x^m\right)(1-x)^n \tag{1}$$

$$k_1 = k_{10} \exp\left(-\frac{E_1}{RT}\right) \tag{2}$$

$$k_2 = k_{20} \exp\left(-\frac{E_2}{RT}\right) \tag{3}$$

where x is the degree of conversion, k_1 and k_2 are reaction rate constants; these rates are function of two different activation energies (E_1 and E_2) and of the pre-exponential factors (k_{10} and k_{20}), m and n are reaction orders, $(m+n)$ being the overall reaction order.

Moreover, an nth order reaction is used to model a polyurethane based system cure kinetics [8].

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(1-x)^n \tag{4}$$

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{5}$$

where k is the reaction rate constant; E is the activation energy and k_0 the pre-exponential factor, n is the reaction order.

Salla et al. [10] studied the curing kinetics of a carboxylate polyester with triglycidylisocyanurate (TGIC) using DSC and temperature modulated DSC (TMDSC). They suggested an autocatalytic kinetic model:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = kx^m(1-x)^n \tag{6}$$

with

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{7}$$

In this last case, kinetic parameters were obtained from different sets of heating rates by DSC and TMDSC. The influence of the experimental conditions on the kinetic parameters was discussed. The chosen kinetic parameters were: $k_0 = 24\ \mathrm{s}^{-1}$, $E = 110\ \mathrm{kJ{\cdot}mol^{-1}}$, $n = 1.9$, $m = 0.1$.

2.2. Physical properties

Another way to study the curing process of powder coatings is to analyse the evolution during curing of such physical parameters as the glass transition temperature (Tg), the viscosity or gel point.

Indeed, powder coatings usually have a Tg around 70 °C and its evolution during curing gives information on the state of the forming polymer and on the value of the conversion [12].

In 2001, Belder et al. [13] determined the four principle stages taking place during the film formation process of a polyester+TGIC powder. They used a combination of techniques (differential scanning calorimetry (DSC) or thermo gravimetry analysis (TGA) and a modified version of DL-TMA (dynamic load thermal mechanical analysis)). The experiments enabled them to determine the melting and gel points and to define the following curing stages:

1st stage: the powder coating is still present as a powder.
2nd stage: this stage begins at the melting point. With this stage begins the melting of the powder coating. The powder coating has the consistency of a viscous liquid.
3rd stage: this is the flow period of the powder coating. The viscosity of the sample decreases rapidly and the polymerisation reactions begin at this stage.
4th stage: in this step, there is a decrease of the heat released by the polymerisation reactions, and the viscosity is very high, the powder coating, which is mostly polymerised, is gelled. The beginning of this stage corresponds with the gel point.

In this work, the extent of reaction at gel point was determined experimentally and calculated; the examination of the results of the study showed that the different curing stages are affected by the type and the level of the coatings components.

Finally, the study of the evolution of the viscosity of the forming polymer is also important as it is correlated to the evolution of the degree of conversion. In 1999, Lee et al. [8] studied the rheological behaviour during the infrared curing under isothermal conditions of epoxy-based and polyurethane-based coating systems. They showed that the evolution of the complex viscosity was correlated with the degree of conversion. In particular, the gelation in both systems occurred at a conversion of 0.45. Their study enabled them to analyse the structure build-up on the surface of the coating. They showed that:

- The surface structure is build-up before the gelation point but continues to evolve after the gelation. The process of the structure build-up varies with the properties of the system (formulation, reaction, and mechanism of structure build-up).
- The surface structure and roughness value do not change significantly during curing.
- The surface roughness does not depend on the cure temperature.

Three-dimensional topography and roughness during curing were observed with a confocal laser scanning microscope. It was thus determined that, in the epoxy-based coating, the fine surface structure develops without any change of roughness value after the coarse structure appears, whereas the fine structure of the surface of the polyurethane-based coating develops suddenly followed by a decrease of the peak-to-peak distances.

Thus, there are many ways to characterise the cure process of powder coatings; the study of physical parameters can be done, and cure kinetics studies of thermosetting powder coatings have been widely described in the literature. Nonetheless, few papers characterise the cure process of powder coatings by correlating thermal modelling of the cure process and kinetics studies [14,15]. This is the aim of the present study, in order to build the basis for a better control of the curing process.

2.3. Infrared curing efficiency

A better control of the curing process will also be realised when we will have determined which type of infrared wave is the most efficient to cure the powders.

The majority of the papers deal with infrared heating using different types of infrared sources, namely short, medium and long wave [16–18]. The efficiency of IR heating depends on both the coating spectral absorption characteristics and the spectral emissions of the infrared source, that is why some publications deal with the measuring of the IR absorptivities of powder coatings.

Carr et al. [16] have studied the IR absorptivities of different powder coatings. A Fourier transformed infrared spectrometer (FTIR) with an integrated sphere was used to measure the powder coating spectral absorptivity of the entire IR spectrum. Using the spectral absorptivities and normalised blackbody emissions, the integrated average absorptivities were calculated for blackbody emitter temperatures ranging from 500 to 3000 K. Both types of absorptivities were determined for powder coatings of different type: polyesters, epoxies, hybrids, and polyurethanes; this to determine the effects of several coating parameters on IR absorption. The parameters considered were polymer type, pigment, film thickness, curing and gloss.

Table 1
Characteristics of the powder used during the study

Chemical data	Composition	Polyester-based powder coating+triglycidylisocyanurate (TGIC 3 to 5%) crosslinker, pigments and various additives
	Particle size	38.0–42.0 µm
	Volumic mass	1590 kg·m^{-3}
Curing conditions	Type of electrostatic powder coating process	Corona spray gun
	Curing type	Electrical infrared
	Curing temperature and curing time	255 °C/105 s
	Typical film thickness	60–80 µm

Deans et al. [17] have also determined the spectral absorptivity (calculated from tests which measured the reflectivity thanks to a FTIR spectrometer fitted with a diffuse reflectance accessory (DRIFT)) of powder coatings of different composition and colour. These measurements have been made during an experimental investigation aimed to determine the efficiency of energy transfer between an infrared gaseous infrared burner and a powder coated surface being cured. They concluded that both powder colour and composition influence the spectral absorptivity of the powder; nonetheless the darker powders (which also absorb more light in the visible range) absorb more infrared energy.

In our study, we will use a simpler method to characterise the infrared curing efficiency and we will examine the infrared efficiency by determining which type of infrared emission leads to the fastest cure.

3. Experimental

3.1. Materials

The powder used during this study was a white thermoset polyester and TGIC system. Its characteristics are summarised in Table 1.

The substrates used during the curing study were steel standard test panels. The dimensions of the panels were 72 by 45 by 1 mm^3. They were degreased with acetone before the application of the powder which was realised with a *GEMA PGC1 corona spray gun*.

3.2. Curing procedure

Powder samples were cured in an infrared oven which had been previously described [19]. It was fitted out with an infrared emitter having 9 interchangeable lamps. The different types of infrared sources are listed in Table 2. The lamps could operate in manual (constant flux) or regulated mode (PID and program of a heating rate). During the curing in the infrared oven, the sample temperature was followed by the mean of a pyrometer *Heiman KT15.82* which is sensitive to the infrared emission emitted from the sample between 8 and 14 µm. The operating temperature range of the pyrometer is 25–300 °C.

Table 2
Infrared lamps characteristics

Lamp type	Lamp voltage [V]	Filament temperature [K]	Wave of maximum emissivity peak [µm]	Lamp wattage [kW]
PHILIPS short infrared (SIR)	230	2500	1.16	1
PHILIPS medium infrared (MIR)	230	1750	1.66	1
PHILIPS near infrared (NIR)	230	2950	0.98	1.5

3.3. Measurements

Cure kinetic studies were carried out using differential scanning calorimetry (*TA instrument DSC2920 modulated DSC*). Non-isothermal measurements were conducted from 25 to 280 °C at a heating rate of 5 or 10 °C·min^{-1}. The conversion or extent of cure was obtained thanks to DSC: it is proportional to the heat of cure that can be obtained experimentally by DSC [8,9] and is given by the following equation:

$$x = \frac{\Delta H_t}{\Delta H_0} \tag{8}$$

ΔH_0 is obtained by integration of the DSC peak between the start and the end of the polymerisation reaction.

ΔH_t is obtained by integration of the DSC peak between the start of the reaction and a time t, whereas x corresponds to the value of the conversion at the time t.

4. Results and discussion

4.1. Cure kinetics

Two experiments were carried out, in which the systems were cured under non-isothermal conditions from 25 to 280 °C at a heating rate of 10 °C·min^{-1}. This was done on one hand to verify the reproducibility of the results, on the other hand to compare the results obtained with powders of the same kind but coming from different batches (A and B types). A third experiment was realised with a heating rate of 5 °C·min^{-1} from 25 to 280 °C. In Fig. 1, the dotted lines represent the evolution of the experimental conversion as a function of the curing time. The superposition of the experimental conversion of A and B powders shows the good reproducibility of this method.

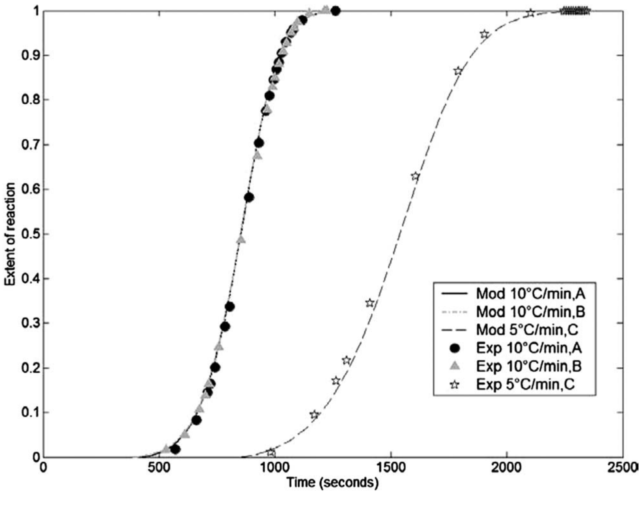

Fig. 1. Reaction kinetics obtained at dynamic temperature.

According to the literature survey [10], the kinetic model that describes the polymerisation of the polyester + TGIC system is an autocatalytic model:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = kx^m(1-x)^n \tag{9}$$

with

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{10}$$

The kinetics parameters n, m, k_0 and E were estimated using the software Matlab and the optimisation toolbox with the algorithm of LEVENBERG–MARQUARDT. The results are summarised in Table 3 whereas Fig. 1 represents the evolution of the experimental and calculated conversion as a function of the curing time.

On Fig. 1, we can see that there is a very good concordance between the experimental points and the model. This is true for each experiment, and indicates that the model describes well the curing process of the polyester + TGIC powder.

What's more, as in [11] and as it is shown in Table 3, the variation of the kinetic parameter values with the heating rate is placed in the experimental error limit (within 10% of the average value). We can therefore conclude that the kinetic parameters do not vary with the heating rate and we will use the mean value of the parameters (Table 3) for our further calculations.

To complete these results, a study of the parameters sensibility was realised. To do so, we made each parameters vary around their optimised value, the other parameters being maintained constant. The influence of this variation is observed on the value of the mean square error sum, which is defined by the deviation between the calculated conversion and the experimental one.

Fig. 2 presents the plot of the mean square error values in function of a deviation of +/−20% from each estimated parameter value. From the shapes of the curves, we can conclude that E is very sensitive, when k_0 and n are quite sensitive and m is not sensitive at all in this experimental work conditions. But, analysing these results, one should keep in mind that, despite the difference of sensibility between E and k_0, these two parameters are not independent variables [20]. Usually the variation of E does not produce any vari-

Table 3
Kinetic parameters obtained with the identification program realised in dynamic mode

	k_0 [s^{-1}]	E [J·mol^{-1}]	n	m
1st batch of powder cured at 10 °C·min^{-1}	4884000	74462	1.2448	0.1147
2nd batch of powder cured at 10 °C·min^{-1}	4846800	74263	1.3048	0.1166
1st batch of powder cured at 5 °C·min^{-1}	4771600	73639	1.2868	0.1
Mean	4834133	74121	1.2788	0.11043333

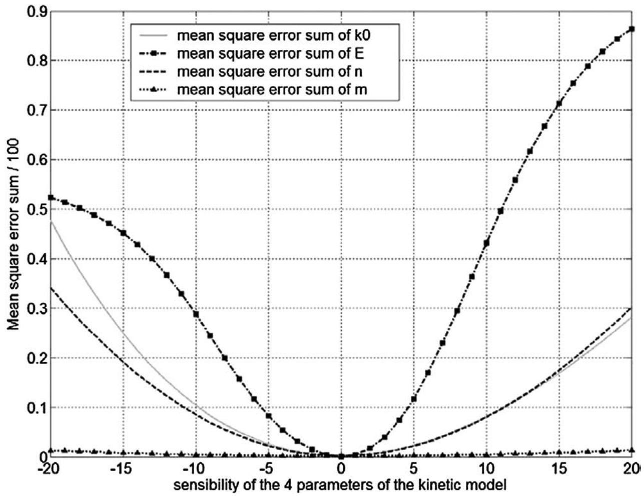

Fig. 2. Sensibility of the 4 parameters of the kinetic model.

ation on the Arrhenius constant k, due to the compensation effect of k_0.

4.2. Thermal modelling

4.2.1. Experimental results

Powder samples, which had been applied on identical metallic substrates, were cured using infrared radiation under a constant flux density of 25 kW·m^{-2}. Samples were taken from the infrared oven at different times, namely 30, 60, 120, 180, 300 seconds, and were analysed by DSC, so that we could determine the conversion at the removal time. One experiment in a steam chamber at 250 °C was also made to use natural convection.

Fig. 5 shows the evolution of the samples' temperature in function of the curing time for each heating mode. We can see that the medium wave infrared emitters lead to the fastest rise of temperature; the other emitters, the short and near wave emitters lead to similar temperature evolution. The kinetic study carried out in parallel shows that the fastest evolution of the conversion is also obtained with the medium wave infrared emitters (Fig. 3).

Four experiments, with constant heating rate were also carried out with the different infrared lamps.

- Maximum heating rate: 1.87 °C·s^{-1};
- Maximum heating rate—10%: 1.68 °C·s^{-1};
- Maximum heating rate—20%: 1.5 °C·s^{-1};
- Maximum heating rate—40%: 1.12 °C·s^{-1}.

As the heating rate is constant for all the infrared emitters, the film temperature was the only parameter influencing the curing kinetics; the type of infrared only favoured more or less the heat transfer. These experiments confirmed the previous results and permitted to conclude on the most effective cure process. The use of Philips medium wave infrared emitters led to the fastest heating rate. The radiative properties of the powder coatings were probably centred on the wavelengths corresponding to the medium wave infrared (1.66 µm).

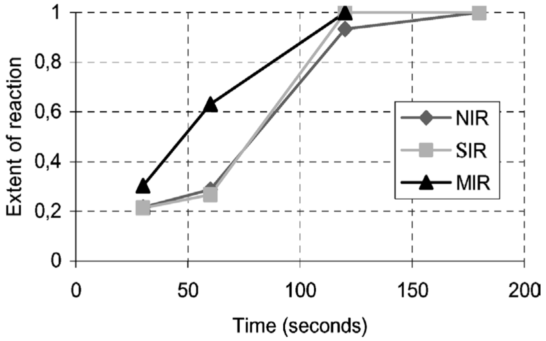

Fig. 3. Conversion evolution when the powder, applied on a metallic substrate, is cured under a flux density of 25 kW·m^{-2}.

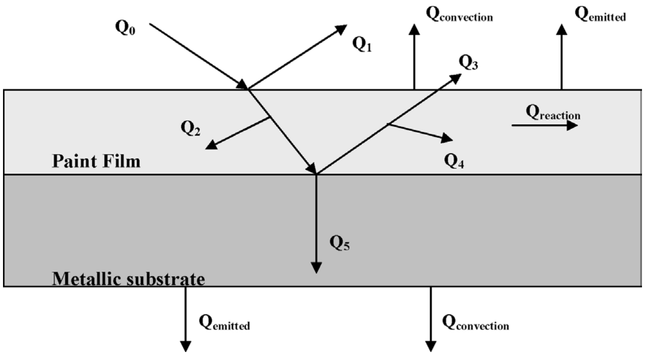

Fig. 4. Thermal balance.

The efficiency of IR heating depends on both the coating spectral absorption characteristics and the spectral emissions of the infrared source.

We believe that medium wave infrared leads to the fastest cure because infrared absorption of the studied powder coating is the most important at this wavelength. In a further work we will try to prove this statement by measuring experimentally the radiative properties of these powders (absorptivity, reflectivity, transmissivity) [16].

4.2.2. Modelling

Our goal was to determine a mathematical model based on the knowledge of the fundamental mechanisms governing thermal transfers so that we would be able to predict the evolution of the film temperature when the powder was under a radiative flux.

The film thickness was small enough and the metallic substrate was quite a good thermal conductor, so that we could consider that the temperature was constant in all the system substrate+paint (this hypothesis had been experimentally verified by measuring the temperature with 2 thermoelectric couples: one stuck under the metallic panel, the other on top of the cured paint. We obtained a maximum difference between the temperatures of 5 °C. Given the precision of the thermocouples (type K, precision 3%), we can consider that both temperatures are equal). Fig. 4 illustrates the thermal balance calculated on our system.

As Blanc [21], we used the following mathematical expression to solve the thermal balance:

$$\frac{\mathrm{d}T}{\mathrm{d}t}(Cp_p\rho_p e_p + Cp_{\mathrm{sup}}\rho_{\mathrm{sup}}e_{\mathrm{sup}}) = Q_{\mathrm{abs}} - Q_{\mathrm{reaction}} - Q_{\mathrm{emitted}} - Q_{\mathrm{convection}}$$

with p and sup representing, respectively, the paint film and the metallic substrate.

- Q_{abs} represents the infrared energy that is absorbed by the 'substrate+paint' system. If we consider that the substrate absorbs all the energy, the thermal balance becomes: $Q_{\mathrm{abs}} = Q_0(1-\rho_p^*) - Q_0\tau_p^2(1-\alpha_{\mathrm{sup}}) = Q_0 - Q_1 - Q_3 = Q_2 + Q_4 + Q_5$, with α_{sup}: substrate absorption coefficient, ρ_p^*: paint reflection coefficient, Q_0: incident radiative flux, Q_2 and Q_4: energy absorbed by the paint film, Q_5: energy absorbed by the metallic substrate, Q_3: energy transmitted by the paint and reflected by the substrate; this term (order two) was supposed negligible for this paint.
- Furthermore, Q_{emitted} represents the energy lost by radiative emission from the two faces of the system; we have $Q_{\mathrm{emitted}} = \sigma\varepsilon_{\mathrm{sup}}(T^4 - T_1^4) + \sigma\varepsilon_p(T^4 - T_2^4)$, with ε_p: paint emissivity, $\varepsilon_{\mathrm{sup}}$: substrate emissivity, σ: Stefan–Boltzmann constant $= 5.670 \times 10^{-8}$ $\mathrm{W{\cdot}m^{-2}{\cdot}K^{-4}}$,
- Q_{reaction} represents the heat released by the exothermic chemical reaction and $Q_{\mathrm{reaction}} = \rho_p e_p \frac{\mathrm{d}x}{\mathrm{d}t}\Delta H_0$, with ΔH_0: enthalpy of the complete reaction in $\mathrm{J{\cdot}kg^{-1}}$ ($-20800\ \mathrm{J{\cdot}kg^{-1}}$); the value of this term was negligible against Q_0 for this paint.
- $Q_{\mathrm{convection}}$ represents the thermal losses due to natural convection from the upper and the lower face of the system: $Q_{\mathrm{convection}} = h_{\mathrm{ai}}(T - T_1) + h_{\mathrm{as}}(T - T_2)$, with h_{ai}: convective exchange coefficient under the substrate, h_{as}: convective exchange coefficient on top of the paint, T_1 and T_2: temperature of the walls under and upper the sample.

The estimations of the convective exchange coefficients are [21]: $h_{\mathrm{ai}} = 3\ \mathrm{W{\cdot}m^{-2}{\cdot}K^{-1}}$ and $h_{\mathrm{as}} = 5.7\ \mathrm{W{\cdot}m^{-2}{\cdot}K^{-1}}$.

The thermophysical properties of the substrate have been found in the literature: $Cp_{\mathrm{sup}} = 460\ \mathrm{J{\cdot}kg^{-1}{\cdot}K^{-1}}$, $\rho_{\mathrm{sup}} = 7800\ \mathrm{kg{\cdot}m^{-3}}$, $e_{\mathrm{sup}} = 1 \times 10^{-3}$ m, $\alpha_{\mathrm{sup}} = 0.8$ for high temperature (Q_0) and $\varepsilon_{\mathrm{sup}} = 1$ for low temperature.

The thermophysical properties of the paint have been fixed to the following values: Cp_p: 1500 $\mathrm{J{\cdot}kg^{-1}{\cdot}K^{-1}}$ measured with the DSC, ρ_p: 1590 $\mathrm{kg{\cdot}m^{-3}}$ (paint supplier technical data), e_p: 80×10^{-6} m, ε_p: 0.91 for low temperature.

Table 4
$\alpha_p + \tau_p$ and ρ_p^* values for each infrared emitter

	MIR	SIR	NIR
$\alpha_p + \tau_p$	0.6	0.4	0.4
ρ_p^*	0.4	0.58	0.55

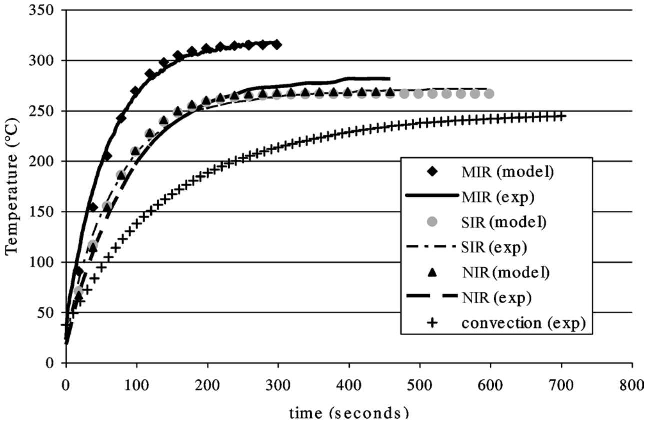

Fig. 5. Experimental and simulated heating rates of the powder deposited on the metallic substrate.

The thermal balance numerical simulation was realised with the Matlab software. Table 4 presents the paint absorption (and transmission) and reflection coefficients values which have been chosen to simulate at best the system heating rate.

Fig. 5 represents the experimental and simulated system heating rates. These results show that the thermal model, though quite simple, permits to satisfactory predict the experimental heating rate. The main improvements should concern the radiative properties of the paints and to a certain extent, those of the substrate. These properties must change during curing in function of the temperature and conversion evolution.

5. Conclusion

This study has enabled us to study the curing of a commercial polyester+TGIC powder.

First, the kinetic parameters of the autocatalytic kinetic model were obtained through non-isothermal experiments realised by DSC.

Secondly, thermal transfers were examined by studying the evolution of the paint film surface temperature when it is cured on a metallic substrate thanks to different infrared emitters: medium, short and near infrared emitters. The study showed that the medium infrared was the most efficient to cure the powder. Moreover, the correlation of thermal modelling of the cure process and kinetics studies enabled us to develop a model predicting the evolution of the temperature, using the hypothesis that the paint film and the substrate are at the same temperature. The paint film radiative properties are still to be determined in function of the temperature and the conversion.

A rheological study should now be made to correlate the thermal and rheological behaviour of the powder with its surface structure build-up; other experiments should also be done to extend the results obtained with the polyester+TGIC powder to other thermosetting powder coatings systems.

Acknowledgements

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References

[1] The position of the paint and printing ink industry, CEPE News janvier 2003—Conseil Européen de l'industrie des Peintures des Encres d'imprimeries et des couleurs d'art.

[2] T.A. Misev, R. Van Der Linde, Powder coating technology: New developments at the turn of the century, Prog. Org. Coat. 34 (1998) 160–168.

[3] R. Bayards, M. Antonisse, Curing pigmented UV powder coatings, European Coat. J. 5 (2002) 557–560.

[4] A. Tinnemans, A. Roescher, Low temperature powder coating: a new UV-curing reaction at moderate temperature, Prog. Org. Coat. 40 (2000) 191–194.

[5] M. Gedan-Smolka, D. Lehermann, S. Cetin, Basic investigations for development of new curing mechanisms for powder coatings, Prog. Org. Coat. 33 (1998) 177–185.

[6] C.U. Böttner, M. Sommerfeld, Numerical calculation of electrostatic powder painting using the Euler/Lagrange approach, Powder Technol. 125 (2002) 206–216.

[7] Q. Ye, J. Domnick, On the simulation of space charge in electrostatic powder coating with a corona spray gun, Powder Technol. 135–136 (2003) 250–260.

[8] S.S. Lee, H.Z.Y. Han, J.G. Hilborn, J.A.E. Manson, Surface structure build-up in thermosetting powder coating during curing, Prog. Org. Coat. 36 (1999) 79–88.

[9] V. Calado, S.G. Advani, Thermosets resin cure kinetics and rheology, in: A. Loos, R. Dave (Eds.), Transport Processes in Composites, 2000, pp. 31–105.

[10] J.M. Salla, X. Ramis, J.M. Morancho, A. Cadenato, Isoconversional kinetic analysis of a carboxyl terminated polyester resin crosslinked with triglycidylisocyanurate (TGIC) used in powder coating from experimental results obtained by DSC and TMDMC, Thermochim. Acta 388 (2002) 355–370.

[11] D. Roşu, C.N. Caşcaval, F. Mustąţă, C. Ciobanu, Cure kinetics of epoxy resins studied by non-isothermal DSC data, Thermochim. Acta 383 (1–2) (2002) 119–127.

[12] X. Ramis, A. Cadenato, J.M. Morancho, J.M. Salla, Curing of a thermosetting powder coating by means of DMTA, TMA and DSC, Polymer 44 (2003) 2067–2079.

[13] E.G. Belder, H.J.J. Rutten, D.Y. Perera, Cure characterisation of powder coatings, Prog. Org. Coat. 42 (2001) 142–149.

[14] R.G. Sahli, J.M. Vergnaud, Testing the kinetic and thermal parameters for the cure of an unsaturated polyester, Thermochim. Acta 285 (2) (1996) 277–288.

[15] V. Antonucci, M. Giordano, K.-T. Hsiao, S.G. Advani, A methodology to reduce thermal gradients due to the exothermic reactions in composites processing, Internat. J. Heat Mass Transfer 45 (8) (2002) 1675–1684.

[16] W.W. Carr, V.A. Williamson, E.G. McFarland, M.R. Johnson, A.L. Stewart, W.E. Pasley, Characterization of infrared absorption by powder coatings on steel panels, J. Coatings Technol. 71 (889) (1999) 71–84.

[17] J. Deans, M. Kogl, The curing of powder coatings using gaseous infrared heaters: An analytical model to assess the process thermal efficiency, Internat. J. Thermal Sci. 39 (2000) 762–769.

[18] K. Bär, La cuisson des peintures en poudres: L'affaire de quelques secondes, Galvano Organo Traitements de Surface 69 (704) (2000) 402, 441–443.

[19] D. Blanc, S. Vessot, P. Laurent, J.F. Gerard, J. Andrieu, Study and modelling of coated car painting film by infrared and convective drying, Drying Technol. 15 (9) (1997) 2303–2323.

[20] S. Vyazovkin, Two types of uncertainty in the values of activation energy, J. Thermal Anal. Calorimetry 64 (2001) 829–835.

[21] D. Blanc, P. Laurent, J.F. Gerard, J. Andrieu, Modelling of reactive infrared drying of a model water-based epoxy-amine painting coated on iron support with experimental validation, in: Proceedings of 11th International Heat Transfer Conference, Kyongju, vol. 5, Korea, August 1998, pp. 181–186.