Progress in Organic Coatings 70 (2011) 186–191

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Thermochemical and isoconversional kinetic analysis of a polyester–epoxy hybrid powder coating resin for wood based panel finishing

Günter Wuzella[a], Andreas Kandelbauer[b,c,*], Arunjunai Raj Mahendran[a], Alfred Teischinger[c]

[a] WOOD Carinthian Competence Center, Kompetenzzentrum Holz GmbH, Klagenfurterstrasse 87-89, A-9300 St. Veit an der Glan, Austria
[b] School of Applied Chemistry, Reutlingen University, Alteburgstrasse 150, D-72762 Reutlingen, Germany
[c] Department of Wood Science and Technology, University of Natural Resources and Applied Life Sciences, Peter Jordan Strasse 82, A-1190 Vienna, Austria

ARTICLE INFO

Article history:
Received 3 June 2010
Received in revised form 3 September 2010
Accepted 3 September 2010

Keywords:
Powder coating
Epoxy–polyester hybrid resin
Isoconversional kinetics
Curing
Differential scanning calorimetry
Rheology

ABSTRACT

Powder coating is an established technology especially for the surface finishing of metallic substrates for example in the automotive industry. Moreover, powder technology holds also great promises for the coating of non-conventional substrates like plastics or wood due to the lack of solvents and good recoverability. Here, low-temperature curing resins are required and especially mild processing conditions are demanded by the substrates. Advanced characterization methods need to be established that allow the precise balancing of the processing conditions required for adequate melting, flowing and curing of the powder with the process conditions that can be tolerated by the temperature-sensitive substrates. In the present contribution it is shown that differential scanning calorimetry (DSC) in combination with isoconversional kinetic analysis (ICKA) provides great potential for this purpose. DSC is a standard thermo-chemical method that can be successfully used to study both the melting and curing processes of powder coatings and to determine, for example the glass transition temperature of the cured coating directly from the measured thermograms. However, still more information can be extracted from the enthalpy signals when more sophisticated methods of data post-treatment and analysis are employed. Isoconversional kinetic analysis techniques such as the Kissinger–Akahira–Sunose (KAS) or the advanced Vyazovkin (VA) approaches allow calculating the time-dependencies of physical and chemical processes at various temperatures based on the estimates of activation energies which are obtained from DSC raw data. These analyses allow for example to calculate the time required for a certain degree of cross-linking in the coating after processing the coating under specified curing conditions. In the present contribution the application of ICKA of DSC measurements for the analysis of the flowing and curing behaviour of a powder coating based on a polyester–epoxy hybrid resin is illustrated and the potential of this approach to predict optimal curing times for arbitrary curing temperatures is demonstrated. This is especially useful when temperature-sensitive substrates like wood-based panels are coated. Additionally, the potential to relate the thermo-chemical properties of the powder coating to the surface properties of the coated substrates is discussed.

1. Introduction

While powder coating [1] of metallic substrates [2] is an industrially well established technology especially in the automotive industry, the application of powder coatings in the surface finishing of non-conventional substrates such as plastics [3], wood panels [4] or natural fibre-based materials [5] is still not very much developed on an industrial scale. Non-ideal material compatibility between coating and carrier as well as rough surface texture, low conductivity and high temperature sensitivity of the substrate represents major obstacles for the successful industrial implementation of such processes. For example, currently, only one major wood-based panel producer manufactures medium density fibre (MDF) boards of a special surface quality which can be readily coated with newly developed low temperature powder resins. Although this technology is currently industrially not yet practicable, powder technology holds great promises in the near future for the coating of non-conventional substrates, mainly because of obvious environmental and economical reasons.

For wood-based panels, especially the pronounced temperature sensitivity of the carrier board represents a challenge and hence, low-temperature curing resins and especially mild processing conditions are demanded. Advanced characterization methods need

* Corresponding author at: Reutlingen University, School of Applied Chemistry, Alteburgstrasse 150, D-72762 Reutlingen, Germany. Tel.: +49 07121 271 2009; fax: +49 7121 271 90 2009.
E-mail address: andreas.kandelbauer@reutlingen-university.de (A. Kandelbauer).

0300-9440/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.porgcoat.2010.09.023

to be established that allow the precise balancing of the processing conditions required for adequate melting, flowing and curing of the powder with the process conditions that can be tolerated by the temperature-sensitive substrates. In the present contribution it is shown that differential scanning calorimetry (DSC) in combination with isoconversional kinetic analysis (ICKA) provides great potential for this purpose. It will be shown that with appropriate model-free kinetic approaches theoretical curing isotherms can be calculated that allow accurate modelling of the chemical cross-linking process during film formation of the powder coating. A priori knowledge of the time required for complete resin cure at arbitrary temperatures is especially helpful when the powder coating process of temperature-sensitive substrates like wood-based panels is envisioned. Based on simple laboratory experiments on a micro-scale processing times that provide degrees of conversion close to 100% for different temperatures can be calculated and it can be evaluated in advance whether these processing times exceed the time during which the wood-based panel tolerates the temperature treatment without structural damage. However, although thermo-chemical characterization of resin curing is necessary for the understanding of the curing process, this knowledge is not yet sufficient for optimizing the overall process conditions and for fully predicting the industrial requirements for defect-free surface film formation. Thermo-chemical parameters derived from DSC need also to be related to rheological parameters of the powder coating which characterize the film formation and leveling properties of the coating. Moreover, the thermo-chemical data need also to be related to the final technological properties of the coated surface to model the overall quality of the powder coating process.

In the present work, two calculation variants of ICKA are compared for their applicability to characterize a polyester–epoxy powder coating and theoretical curing isotherms are calculated based on conversion dependent activation energy profiles. For a pre-defined maximum curing temperature, treatment times for the development of defined cross-linking degrees were calculated using ICKA and related to the solvent resistance of the partially cured powder coating.

2. Theory

All mathematical approaches to describe the temperature dependence of the reaction rate for a specific chemical reaction are based on the fundamental rate equation introduced by Arrhenius [6]. Based on the Arrhenius equation, progress of a chemical reaction is described by three kinetic parameters, the pre-exponential factor, A, the activation energy, E_a, and the reaction model, $f(\alpha)$. Classical kinetic analysis based on the Arrhenius approach requires a priori knowledge on the reaction mechanism and hence is model-dependent. However, the curing of powder coating resins is rather a complex multi-step process than a simple chemical reaction of quantitatively known mechanism. Furthermore, melting and flow processes interfere with the actual cross-linking of the resin. Hence, classical model-dependent kinetic analysis is not suitable to predict the curing kinetics because the exact reaction model is usually unknown. For such complex processes model-free kinetic or so-called isoconversional methods have been developed [7–12] which assume that the effective activation energy at a particular degree of curing α is independent of the temperature program (isoconversional principle). They can be divided in differential and integral methods [13]. In the current work, two integral methods, the Kissinger–Akahira–Sunose (KAS, [10,11]) and the Vyazovkin in its advanced form (VA, [12]), were used to predict the dependence of the effective activation energy on the degree of curing, $E_a(\alpha)$, for a polyester–epoxy hybrid resin based powder coating.

All integral methods are based on the isoconversional principle implying that for any heating rate β the integral form of the reaction model $g(\alpha)$ is constant according to equation (1).

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T} \exp\left(\frac{-E(\alpha)}{RT}\right) dT = \frac{A}{\beta} I[E(\alpha), T] \qquad (1)$$

The various integral methods differ in the way how the temperature integral (I) in Eq. (1) is solved. Whereas older approaches like the KAS method use a specific, fixed approximation of the temperature integral, the more modern VA method enables flexible selection of an appropriate approximation and hence newly developed, improved algorithms may be introduced.

The KAS-approach for solving Eq. (1) is the use of the temperature integral approximation of Doyle [14]. The KAS-approach encompasses a linear regression for each given curing rate α with pairs of values $\ln(\beta)/T^2$ vs. $1/T$ from the corresponding $\alpha(t)$-curves of the heating rates (curves of at least 3 heating rates are necessary) according to

$$\frac{\ln(\beta)}{T^2} = \frac{-E_\alpha}{R} \frac{1}{T} + A' \qquad (2)$$

where β is the heating rate of a DSC measurement in $\mathrm{K\,min^{-1}}$, T is the absolute temperature in K, E_α is the apparent activation energy in $\mathrm{J\,mol^{-1}}$ for the given curing conversion α, R is the gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$) and A' is a complex term comprising the apparent pre-exponential factor A and the integral form $g(\alpha)$ of the reaction model $f(\alpha)$. Without the need of knowing (A') the apparent activation energy for each given conversion can be easily calculated from the slope (k) of the regression for each given conversion ($k = -E_\alpha/R$ in Eq. (2)).

The VA-approach also takes account of the isoconversional principle that for any heating rate β the integral form $g(\alpha)$ is constant and E_α is determined by iteration and minimizing

$$\sum_{i=1}^{n} \sum_{j \neq 1}^{n} \frac{I[E_a(\alpha), T]_i \beta_j}{I[E_a(\alpha), T]_j \beta_i} \qquad (3)$$

One advantage of the VA-approach is, that it is not fixed on using a special approximation of the temperature integral (I). Therefore newly developed and better approximations can be used without changing the VA-approach. With the calculated $E(\alpha)$-curves the time (t_α) required for a certain degree of curing α of the coating at an arbitrary isothermal temperature (T_0) can be estimated [15] using the

$$t_\alpha = \frac{\int_0^T \exp(-E_a(\alpha)/RT) dT}{\beta \exp(-E_a(\alpha)/RT_0)} \qquad (4)$$

3. Materials and methods

3.1. Chemicals

The powder coating studied in this paper was a commercial low-temperature curing powder coating, Drylac Wood 530 (Tigerwerk Lack- und Farbenfabrik GmbH & Co. KG., Austria), which is based on a polyester–epoxy hybrid resin and designed for coating of temperature sensitive wood substrates.

3.2. Differential scanning calorimetry analysis

The degree of resin curing α was calculated from thermograms obtained from measurements with a Mettler-Toledo (Greifensee, Switzerland) 822e differential scanning calorimeter (DSC) and the measured change of exothermal enthalpy was related to the degree of resin curing. The enthalpy changes were recorded and integrated over the range of exothermal enthalpy changes (from time t_{start}