Using Isoconversional Kinetic Analysis of Liquid Melamine–Formaldehyde Resin Curing to Predict Laminate Surface Properties

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ABSTRACT: The curing kinetics of a liquid melamine–formaldehyde impregnation resin were analyzed with differential scanning calorimetry, and the conversion-dependent activation energy for melamine–formaldehyde curing was estimated with the isoconversional model-free kinetic approach developed by Vyazovkin. The conversion-dependent activation energy was used to extend the predictive power of a response surface model describing the influence of some processing factors (press time and resin composition) in the manufacturing of particleboards coated with melamine–formaldehyde-impregnated papers. By substituting the factor "press time" in an RSM established for a press temperature of 170 °C by the factor "conversion" which is accessible from thermo-chemical analysis, additional information on temperature was incorporated into the model. Model applicability for additional temperatures was evaluated with 12 validation experiments. Although chemical resistance was difficult to model, cleanability was sufficiently well described by only one factor (conversion). Surface gloss depended on both the conversion and catalyst amount and was predicted by a two-factor interaction model ($R^2 = 0.95$). This study demonstrates that parameters derived from the isoconversional kinetic analysis of liquid resins not only are theoretical descriptors but also have direct practical relevance in the modeling of product properties derived from these liquid resins when used to supplement technological databases. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2649–2660, 2009

Key words: activation energy; curing of polymers; differential scanning calorimetry (DSC); modeling; thermosets

INTRODUCTION

In 2006, approximately 1 million metric tons of melamine was consumed by the wood-based panel industry for furniture and construction materials; the consumption is projected to reach 1.3 million tons by 2009.[1] Although only minor fractions of the total melamine production volume were used for surface coatings (9%), molding compounds (7%), and other applications, about 30% was transformed into gluing resins for engineered wood. However, the major fraction was used for melamine–formaldehyde (MF) impregnation resins for industrial laminates (ca. 50%).[1] Decorative laminates are cheaper substitution products for solid wood boards and consist of carrier materials that are coated with MF-impregnated decorative papers. Typical carrier materials are fiberboards or particleboards in the case of low-pressure melamine films or stacks of kraft papers impregnated with a phenol–formaldehyde resin in the case of high-pressure laminates. The MF-impregnated decorative surface layer is visually attractive with a woodlike or other customized design, and it protects the surface from mechanical damage (scratch and abrasion resistance), chemical attack, and hot objects. Moreover, the excellent cleanability of MF surfaces confers good hygienic properties as well.[2]

Although melamine–urea–formaldehyde copolymerizates have been suggested for use in laminates,[3–5] the predominantly used resin type is MF, which combines several good material properties: water-based MF resins are relatively simple to prepare and handle and form smooth surface films on the carrier boards, allowing even the postforming of three-dimensionally curved surface geometries. Because the resins are not completely cured but remain reactive in impregnated sheets, the sheets are self-gluing, and no additional glue is required in the

thermofusing process. Cured MF films are sufficiently hard and display high resistance against temperature, chemicals, and hydrolysis, and this makes them suitable for interior working surfaces and, when duly protected by light stabilizers, highly durable exterior cladding materials. MF resins are not colored, and paper sheets impregnated with MF are transparent. This is a prerequisite for brilliant surface decoration with impregnated paper décors of various printed designs and for surface protection with transparent cover sheets containing corundum.[6]

The major factor influencing the surface quality of laminates is the curing behavior of the impregnated paper and the achieved degree of MF crosslinking. Essential for a good surface is uniform and defect-free curing of the resin film. If the resin is not sufficiently cured during lamination, the coating will lack hardness, durability, brilliance, and resistance toward hydrolysis and chemical agents. On the other hand, if the degree of crosslinking is too high upon paper impregnation, adhesion of the sheet to the composite panel surface will be insufficient, leading to delamination, inferior film flexibility, and unsatisfactory surface quality. Thus, to flexibly tailor specified product properties of wood panels coated with decorative papers, the curing behavior of the MF resin during the manufacturing of the impregnated paper needs to be optimized.

Laminate formation is performed in hot presses at temperatures around 170°C for contact times ranging from less than 1 min in short-cycle presses up to several minutes in multiplaten presses. Press equipment may be in use for several decades, and this can lead to a broad spectrum of industrial equipment in use. Product properties depend strongly on the pressing conditions. Suppliers of impregnated paper hence must be able to deliver products suitable for all types of equipment, processes, and products used by their customers. For the resin technologist, it is extremely important to know how to design impregnation solutions complying with the product requirements, the available production technology, and the production speed.

A key issue in tailoring the curing behavior of MF resins is having the right type and amount of a suitable curing catalyst. To obtain optimal film properties within the shortest possible time range, it must be known in advance what degree of crosslinking can be obtained with a certain combination of MF and catalyst at a specified reaction time and temperature and how this degree of crosslinking relates to the relevant technological surface properties.

In principle, such information is generally obtainable from kinetic studies that, based on a mechanistic reaction model, relate the concentrations of reactants and products to reaction conditions such as the temperature and pH and allow the derivation of quantitative time-dependent concentration profiles of the involved species. In the case of resin curing, however, such an exact reaction model is usually not known because of the complexity of the crosslinking process. Although the general reactions taking place during MF resin formation appear rather simple,[7] the condensation is very complex and strongly dependent on reaction parameters such as the molar ratio, pH, and temperature profile during resin preparation.[8] The numerous possibilities for recombination of the various chemical species lead to very complex reaction mixtures. In such multistep processes, model-free approaches based on isoconversional kinetics are preferable.[9]

Although originally developed for the analysis of thermogravimetric data,[10–12] isoconversional approaches have been applied to describe the kinetics of a wide variety of complex chemical processes such as the dehydration of swollen poly(acrylic acid) hydrogels[13] and combustion and thermal degradation processes,[14–16] and reviews on the application of the method have recently been published.[17,18] This method has recently attracted increasing interest for the kinetic analysis of the crosslinking of resins such as epoxy,[19–21] lignin-based,[22] phenol–formaldehyde,[22,23] and MF resins.[24] The advanced method developed by Vyazovkin[25] was recently shown to be well suited for MF.[24]

In this contribution, the isoconversional approach by Vyazovkin is applied to the model-free kinetic (MFK) analysis of the curing of a liquid MF resin. The theoretical curing isotherms obtained from isoconversional analysis are then used to predict the surface properties (chemical resistance, cleanability, and gloss) of particleboards coated with MF-impregnated decorative papers by the incorporation of values for MF conversion at different temperatures into an existing technological response surface model (RSM).[5]

Several reports have been published that successfully relate the chemistry of formaldehyde-based gluing resins to the technological properties of wood-based composites such as particleboards.[26–28] The methods have included ^{13}C-NMR analysis of liquid urea–formaldehyde,[26] MF,[27] and melamine–urea–formaldehyde resins[28] and have allowed the derivation of mathematical correlations between the ^{13}C peak ratios and the physical properties of the resins in the hardened state in glued boards, such as the mechanical strength, formaldehyde emission, thickness swelling, and crystallinity percentage. However, to the best of our knowledge, no connections have been made between the kinetic analysis of liquid resins and actual technological properties of products made thereof in publications on the isoconversional kinetic analysis of thermochemical data. However, to the engineer, it is important to

link the rather theoretical analysis and calculation of the activation energy, conversion, and isotherms to the practical issue of designing the manufacturing process and optimizing the production conditions. In this study, an attempt is made to achieve this connection between theory and practice. Data derived from MFK are used to increase the applicability range of a model for the prediction of the surface properties of decorative laminates. It is shown that through the use of the MFK-derived conversion of resin cure instead of temperature-dependent parameters such as the press program in the factor analysis of response surface methodology, more generally applicable causal conclusions can be drawn from lamination experiments. Moreover, the number of tedious laboratory-scale impregnation and hot-pressing experiments can be drastically reduced by the inclusion of thermochemical data in technological RSMs instead of the performance of technological experiments at a vast set of different temperatures.

EXPERIMENTAL

Chemicals

The MF precondensate had a melamine/formaldehyde ratio of 1 : 1.9, a solid content of 52%, a water tolerance of 150%, and a viscosity of 27 s, as determined with a flow-cup viscosimeter according to the DIN EN ISO 2431 standard. The catalyst was a complex of morpholine with *para*-toluenesulfonic acid. The decorative paper used in this study was a white design of 70 g/m^2 typical for decorative work surfaces in kitchen and bathroom furniture; it was supplied by Munksjö Paper Decor GmbH & Co. KG (Aalen, Germany).

Differential scanning calorimetry (DSC)

All thermograms were recorded with a model 822e differential scanning calorimeter from Mettler–Toledo (Greifensee, Switzerland).

For dynamic DSC experiments, the MF resin was combined with a catalyst [0.1, 0.3, or 0.5% (w/w)] directly before the recording of the thermogram. To suppress the evaporation of water and other volatiles during condensation, 2.0–3.5 mg of each of the resin samples was weighed in high-pressure, gold-coated stainless steel crucibles (30 μL), which were sealed and subjected to a temperature gradient ranging from 25 to 250°C with five heating rates (2, 5, 10, 15, and 20°C/min). The enthalpy changes were recorded and analyzed for the peak maximum, the onset temperature, and the normalized enthalpy integral (H) with the STAR 8.10 software package (Mettler–Toledo). All experiments were repeated twice.

Analysis of the thermochemical data

From H of the thermograms, both the conversion (α) and the change in the conversion with time [α(t)] were determined at a specific cure time (t). The conversion rate [dα(t)/dt] was obtained by the division of the peak height at time t (dH/dt) by the total enthalpy of the curing reaction (ΔH$_0$).

The α(t) value was calculated as the ratio of the enthalpy released up to time t [ΔH$_p$)$_t$] to ΔH$_0$ according to eqs. (1) and (2):

$$\alpha(t) = (\Delta H_p)_t / \Delta H_0 \qquad (1)$$

$$d\alpha(t)/dt = (dH/dt)/\Delta H_0 \qquad (2)$$

For kinetic analysis, the STAR software package[25,29] was used. All calculations were performed with the advanced Vyazovkin method.[25] In the following section, the theory behind the MFK approach of Vyazovkin is briefly summarized.

Isoconversional kinetic analysis

All mathematical approaches to describing the curing kinetics of thermosets are based on a fundamental rate equation that relates α(t) at a constant temperature (T) to a function of the concentration of the reactants [f(α)] through a rate constant (k$_T$):

$$(d\alpha/dt)_T = k_T f(\alpha) \qquad (3)$$

The temperature dependence of the rate constant follows the Arrhenius relationship:

$$k(T) = A \exp(-E_a/RT) \qquad (4)$$

where A is the pre-exponential factor or Arrhenius frequency factor (s^{-1}), E$_a$ is the activation energy (J/mol), R is the gas constant (8.314 J/mol K), and T is the absolute temperature of the sample (K).

To account for the temperature dependence of α, the kinetic model is combined with the Arrhenius equation, and the reaction progress is expressed as follows:

$$d\alpha/dt = A \exp(-E_a/RT) f(\alpha) \qquad (5)$$

When the reaction mechanism is known, the reaction model f(α) can be derived and, if E$_a$ is constant throughout the reaction, expressed as a function of the concentrations of the various components involved. However, with complex chemical reactions, the reaction model is often not known, and the special case of E$_a$ ≠ f(α) strictly applies only for very simple or elementary reactions. With more complicated reactions, E$_a$ for the overall process contains contributions of side or consecutive reactions,

and the assumption of $E_a \neq f(\alpha)$ is not valid. In such cases, MFK methods preferably should be used.

All MFK approaches are based on the isoconversional principle.[17,18] Taking the logarithm of eq. (5) and differentiating with respect to T^{-1} lead to

$$\ln d\alpha/dt = \ln A - E_a(\alpha)/RT + \ln f(\alpha) \qquad (6)$$

$$d(\ln d\alpha/dt)/dT^{-1} = d \ln A/dT^{-1} - E_a(\alpha)/R \\ + d \ln f(\alpha)/dT^{-1} \qquad (7)$$

where $E_a(\alpha)$ is the conversion-dependent activation energy. In the isoconversional assumption, the terms $d \ln A/dT^{-1}$ and $d \ln f(\alpha)/dT^{-1}$ at a constant conversion are zero, and the relation can be simplified to

$$d(\ln d\alpha/dt)/dT^{-1} = -E_a(\alpha)/R \qquad (8)$$

Because $d \ln f(\alpha)/dT^{-1}$ equals 0, no *a priori* knowledge of the reaction mechanism is required, and errors due to wrong reaction model selection are avoided. The reaction rate at a certain value of α ($d\alpha/dt$) depends only on the temperature. Another important feature is that with MFK methods, E_a is determined with respect to the conversion as $E_a(\alpha)$.

Several isoconversional methods have been developed to find the $E_a(\alpha)$ function on the basis of eq. (5) in its integral form:[25,30–35]

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^t \exp\left(\frac{-E_a(\alpha)}{RT}\right) dt = AJ[E_a(\alpha), T] \qquad (9)$$

where $g(\alpha)$ is the integral form of the reaction model $f(\alpha)$ and $T(t)$ is the heating program. With a linear heating rate of $\beta = dT/dt$, $T(t)$ is linear, and in eq. (9), dt can be substituted by dT/β:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E_a(\alpha)}{RT}\right) dT = \frac{A}{\beta} I[E_a(\alpha), T] \qquad (10)$$

Solving the temperature integral (I and J) is crucial to all integral methods. Because it has no exact analytical solution,[36] many authors have developed numerical approximations, and the results for MFK analysis of thermochemical data differ widely, depending on the choice of the numerical approach.[34,37–41] To avoid this dependence on the numerical approximation, Vyazovkin and Dollimore[29] used the fact that for any heating rate β, $g(\alpha)$ is constant. Thus, with heating rates β_1, β_2, and β_3, three integrals are obtained [$g(\alpha)_{\beta1} = g(\alpha)_{\beta2} = g(\alpha)_{\beta3}$]:

$$\frac{A}{\beta_1} I[E_a(\alpha), T]_1 = \frac{A}{\beta_2} I[E_a(\alpha), T]_2 = \frac{A}{\beta_3} I[E_a(\alpha), T]_3 \qquad (11)$$

Consequently, A can be truncated, and six equations can be formulated:

$$\frac{J[E_a(\alpha), T]_1 \beta_2}{J[E_a(\alpha), T]_2 \beta_1} = 1 \qquad (12a)$$

$$\frac{J[E_a(\alpha), T]_2 \beta_1}{J[E_a(\alpha), T]_1 \beta_2} = 1 \qquad (12b)$$

$$\frac{J[E_a(\alpha), T]_1 \beta_3}{J[E_a(\alpha), T]_3 \beta_1} = 1 \qquad (12c)$$

$$\frac{J[E_a(\alpha), T]_3 \beta_1}{J[E_a(\alpha), T]_1 \beta_3} = 1 \qquad (12d)$$

$$\frac{J[E_a(\alpha), T]_2 \beta_3}{J[E_a(\alpha), T]_3 \beta_2} = 1 \qquad (12e)$$

$$\frac{J[E_a(\alpha), T]_3 \beta_2}{J[E_a(\alpha), T]_2 \beta_3} = 1 \qquad (12f)$$

which can be summarized as

$$\sum_{i=1}^n \sum_{j \neq 1}^n \frac{I[E_a(\alpha), T]_i \beta_j}{I[E_a(\alpha), T]_j \beta_i} = 6 \text{ for } n = 3 \qquad (13)$$

With the original Vyazovkin method, E_a is determined by iteration and minimization of eq. (13). For example, in the case of three heating rates, the minimum approaches six. This enables free selection of both the temperature integral approximation and the integration limits. Because the regular integration from 0 to T_α (the sample temperature T at a certain conversion x) is used, single values for E_a are averaged over the region of $0 - \alpha$, and the function $E_a(\alpha)$ contains a systematic error[35] that can be avoided by replacement of the regular integration by integration over small time segments (the advanced Vyazovkin method):[25,35]

$$J[E_a(\alpha), T] = \int_{t_\alpha - \Delta\alpha}^{t_\alpha} \exp\left(\frac{-E_a(\alpha)}{RT}\right) dt \qquad (14)$$

The reaction time when the curing has progressed to $\alpha(t_\alpha)$ is calculated as follows:

$$t_\alpha = \frac{\int_0^T \exp\left(\frac{-E_a(\alpha)}{RT}\right) dT}{\beta \exp\left(\frac{-E_a(\alpha)}{RT_0}\right)} \qquad (15)$$

With eq. (15),[42] the $\alpha(t)$ diagrams for an arbitrary isothermal temperature (T_0) can be calculated.[42]

Experimental design

To create a technological RSM that quantitatively describes the effects of some processing variables on

the technological properties of particleboards coated with MF-impregnated papers, a two-factor, five-level full factorial experimental design was performed.[5,43] The varied factors were the catalyst amount (five levels: 0.1, 0.2, 0.3, 0.4, and 0.5% with respect to the weight of the resin solution) and the pressing time (five levels: 8, 10, 12, 16, and 20 s). In this set, the pressing temperature was not varied (press plate temperature = 170°C). A total of 25 different types of boards for each resin mixture and press program were produced. Each experimental setting was repeated twice for statistical reasons. The statistical evaluation of the experimental data set and generation of the response surface diagrams[44] were performed with the computer program Design Expert 6.0.7 (Stat Ease, Inc., Minneapolis, MN).

Preparation of the paper samples

Paper sheets (30 × 30 cm^2) were manually impregnated with an MF resin (ca. 50% solid content) containing different amounts of a curing catalyst and additives (release agent concentration <2%, antifoam agent concentration <0.5%, and surfactant concentration <1.5%). In contrast to industrially manufactured papers, which are impregnated in a two-step process, all laboratory papers prepared for this study were impregnated and coated in a single step with the same MF formulation for core impregnation and surface film formation. Impregnation was performed with a laboratory impregnation device (Munksjö Paper Decor GmbH & Co. KG) with a 0.5-mm doctor blade and an electric propulsion control. The haul-off speed of the paper was 3 m/min, which was sufficiently slow to allow for complete core impregnation and to produce smooth surface films without defects for all prepared samples. Impregnated paper sheets were oven-dried for 90 s at 130°C. After they were dried, the paper weight and humidity were controlled. All papers were coated with 100 ± g/m^2 resin to a final dry weight of about 170 g/cm^2. The final moisture content after drying was 6 ± 0.5%. Then, the paper sheets were wrapped in thermoplastic foil to prevent moisture equilibration with the environment and kept in a conditioning room at 25°C and 50% relative humidity until pressing. Papers were never stored longer than 2 days.

Preparation of the boards

All sheets were pressed onto 7-mm-thick particleboards in a short-cycle laboratory press (Robert Bürkle GmbH, Freudenstadt, Germany) at 35 N/cm^2 for various time periods at a press plate temperature of 170°C (experimental design papers) or at 165 and 175°C (validation papers).

Testing of the boards

Standardized surface quality tests were used to characterize the technological performance of the manufactured boards. Surface gloss was determined as the average of 10 measurements per board of the specular reflectance at an angle of 60°. Cleanability in terms of surface porosity was visually judged under a microscope after an area of 25 cm^2 was tinted with a soft pencil and the pencil marks were rubbed out with an eraser, and the remaining dark dots were counted. The surface was classified on an arbitrary scale ranging from (1) very good (no remaining pencil stains) to (5) very bad (large areas of remaining pencil) in 0.5-unit intervals. The resistance of the boards toward chemical attack was similarly evaluated under a microscope with the acid value (AV). AV was determined by the treatment of a defined surface spot with concentrated hydrochloric acid for 15 min. Afterwards, the surface was microscopically classified according to an arbitrary scale ranging from (1) very good (no attack on the surface by the acid) to (5) very bad (complete destruction of the surface) in 0.5-unit intervals.

RESULTS AND DISCUSSION

To correlate the calculated thermochemical parameters of the liquid impregnation resins from DSC analysis with the technological surface properties of laminated boards, four subsequent experimental steps were performed: (1) determination of thermochemical parameters of various liquid impregnation resins with dynamic DSC and MFK analysis, (2) response surface modeling of technological board properties, (3) incorporation of theoretical kinetic parameters into response surface analysis and generation of a modified predictive model, and (4) validation of the modified predictive model.

In the first step, liquid MF impregnation resin mixtures containing different amounts of the curing catalyst were analyzed by dynamic DSC, and their curing behavior was characterized with kinetic parameters derived from an MFK analysis of the thermochemical data by the Vyazovkin method. From this data set, conversion–time profiles of resin cure were calculated for arbitrary temperatures.

In the second step, decorative papers were impregnated with the same MF resin mixtures and laminated onto particle boards in a hot press for various press times but at the same press plate temperature of 170°C. Certain technological properties of the MF film surfaces—gloss, cleanability, and chemical resistance—were determined, and a mathematical model of the technological properties with respect to the press time and catalyst concentration was calculated.
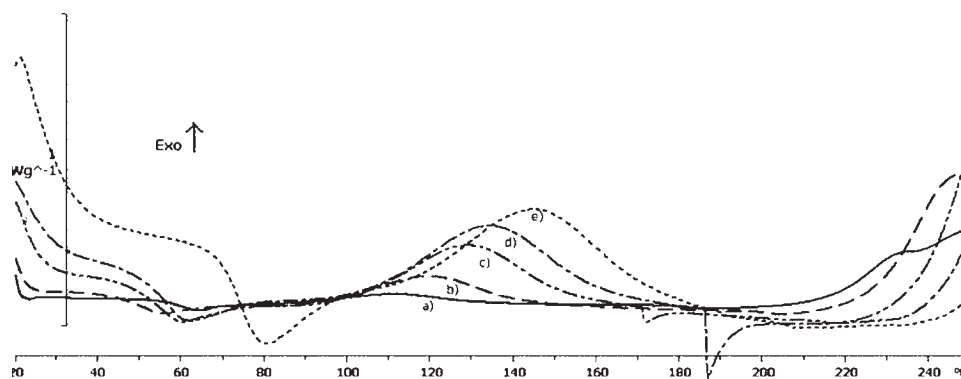
Figure 1 Typical DSC thermograms of an MF resin from an MF resin/catalyst mixture at different heating rates: (a) 2, (b) 5, (c) 10, (d), and (e) 20°C/min.

In the third step, the thermochemical data from step 1 were combined with the RSM of the technological data from step 2. Because the press times and catalyst concentrations were varied systematically, each laminated board contained an MF resin of a different degree of conversion at the specific press temperature. By the assignation to each experimental setting of a theoretical degree of conversion calculated from the independent thermochemical data set derived from DSC, a new RSM was calculated on the basis of the conversion. This modified model now included the influence of temperature on the surface properties and was used to predict the surface quality of boards prepared at different temperatures that were not used to calculate the initial technological RSM.

In the fourth step, validation experiments were performed with the same impregnation resin formulations for impregnation, but the corresponding laminates were pressed at additional temperatures (165 and 175°C). The residuals of the modified model were compared to the experimental error of the validation experiments, and its predictive power was evaluated.

DSC and MFK analysis

Figure 1 shows typical thermograms obtained by dynamic DSC for the curing of an MF resin subjected to a linear increase in the temperature at various heating rates. The initial increase in the exothermal enthalpy at time t_0 indicates the start of resin crosslinking and corresponds to $\alpha = 0$. After reaching a maximum, the enthalpy decreases until curing is practically completed at time t_∞. Although the ideal case of complete curing of the resin is never obtained because of factors such as early immobilization of the condensation network, diffusional hindrance toward the end of the reaction, and cycle-forming reactions that certainly occur at the reaction temperatures used, for the subsequent cal-

culations, the assumption is made that at time t_∞, $\alpha = 1$ is reached. Therefore, minimal deviations of the calculated conversion from the experimental values may be introduced.

Table I summarizes some thermochemical parameters obtained from the thermograms at a heating rate of 10°C/min. The pH of the MF solutions and the curing times measured in test tubes are also given in the table. The initial pH of the impregnation solution and curing time decreased as the catalyst concentration was raised, and the peak temperature and onset temperature shifted toward lower temperatures, whereas H remained constant around 60 kJ/mol. This illustrated that the curing rate was accelerated by an increase in the catalyst concentration without the overall crosslinking potential of the resin being influenced.

From the exothermic enthalpy integrals, $\alpha(t)$ was derived. In Figure 2, $\alpha(t)$ is plotted versus the temperature during the recording of the thermogram at five heating rates. The data from the $\alpha(t)$ curves were used as the basis for isoconversional kinetic analysis.

Figure 3 shows a plot of the values for $E_a(\alpha)$ of MF resins containing different amounts of the curing catalyst; $E_a(\alpha)$ was calculated with the advanced form of the Vyazovkin model with respect to α. It is

TABLE I
Characteristic Curing Parameters of the MF Resin

Catalyst concentration (wt %)	H (J/g)	T_p (°C)[a]	T_o (°C)[b]	pH	t_c (min)[c]
0.1	62	134	121	7.8	7.8
0.3	62	126	108	7.7	5.4
0.5	60	117	100	7.5	3.2

[a] Peak temperature at a heating rate of 10°C/min.
[b] Peak onset temperature at a heating rate of 10°C/min.
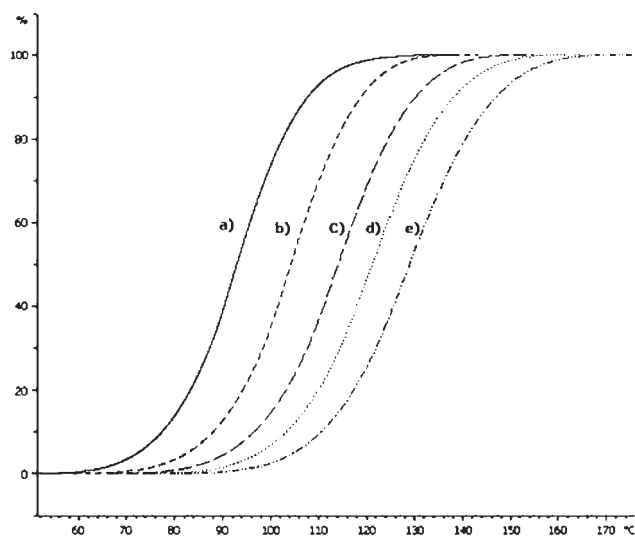[c] Curing time measured in a test tube.

Figure 2 Temperature dependence of $\alpha(t)$ of an MF resin/catalyst mixture at different heating rates during the recording of thermograms (the temperature was that in the DSC vessel, and it was equivalent to a timescale): (a) 2, (b) 5, (c) 10, (d) 15, and (e) 20°C/min.

obvious that $E_a(\alpha)$ was not constant throughout the curing of MF but depended on α and decreased toward the end of the reaction. $E_a(\alpha)$–α profiles strongly depend on the type of catalyst and the mathematical model used for calculation. For example, in an earlier study[24] with a different MF curing catalyst, such a decrease in $E_a(\alpha)$ was observed only with $30\% < \alpha < 40\%$. With $\alpha < 30\%$, $E_a(\alpha)$ was relatively constant (at ca. 74 kJ/mol) and independent of the amount of the catalyst. With $\alpha > 40\%$, $E_a(\alpha)$ slightly increased again until $\alpha = 90\%$ before $E_a(\alpha)$ very sharply increased until curing was completed.[24] Hence, the observed $E_a(\alpha)$ profiles were totally different.
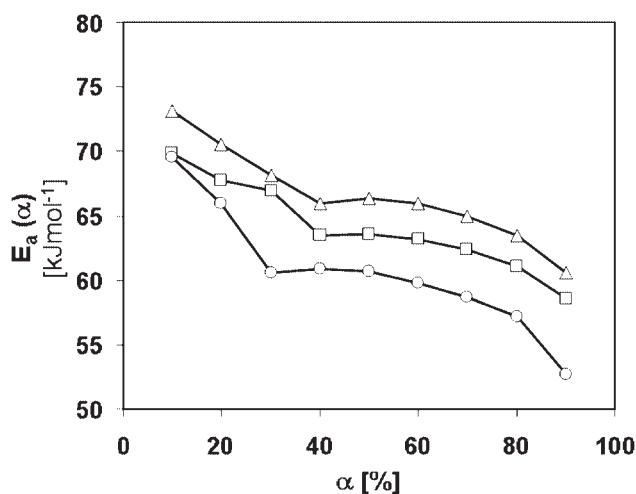

Figure 3 $E_a(\alpha)$ (kJ/mol), calculated with the advanced Vyazovkin method, for an MF resin with a curing catalyst concentration of ($\triangle$) 0.1, ($\square$) 0.3, or ($\bigcirc$) 0.5%.
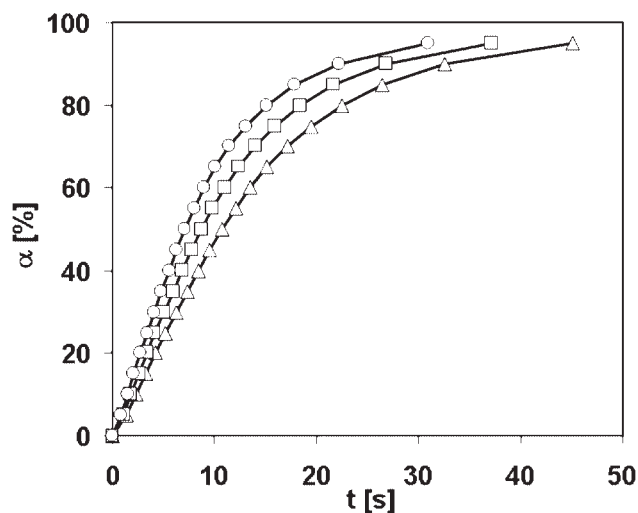

Figure 4 $\alpha(t)$ versus time t for a 0.3% catalyst mixture at ($\triangle$) 165, ($\square$) 170, and ($\bigcirc$) 175°C, as derived from $E_a(\alpha)$ calculated with the advanced Vyazovkin method.

As evident from Figure 3, higher catalyst levels lead to a decrease in E_a. However, this too is not necessarily so. In an earlier study, it was observed that with increased catalyst concentrations, higher values for $E_a(\alpha)$ were calculated, although the overall $E_a(\alpha)$ profiles were very similar and the isotherms calculated thereof fitted the experimental curves well enough.[24] Hence, although $E_a(\alpha)$ profiles calculated with MFK in many cases have been shown to yield valuable mechanistic insights into crosslinking and other reactions,[17] comparisons of different resin systems may be difficult.[9,17]

With the $E_a(\alpha)$ profiles, theoretical isotherms were calculated for the different catalyst/resin mixtures. It was shown earlier for different MF resin/catalyst systems that isotherms for MF curing calculated from $E_a(\alpha)$ values with the Vyazovkin method agreed well with isothermal experiments.[24] Figure 4 shows calculated isotherms at 165, 170, and 175°C derived from $E_a(\alpha)$ for the 0.3% catalyst mixture. The selected reaction temperature/reaction time range was selected because it is suitable for discussing processes taking place during lamination in short-cycle presses for which pressing times below 1 min are used. The isotherms were used to supplement the RSM discussed in the next section and to define a set of validation experiments.

RSM of technological properties

In response surface analysis, theoretical values for a certain technological target property (i.e., response) are calculated with a regression model that is based on the experimental factors which have a statistically significant influence on this response. The analysis of variance (ANOVA) results for the RSM analysis

	AV		P		G	
	F	P > F	F	P > F	F	P > F
Model	29.68	<0.0001	21.01	<0.0001	714.12	<0.0001
[A]	51.68	<0.0001	26.10	<0.0001	1345.45	<0.0001
[B]	7.69	0.0071	15.92	0.0002	82.79	<0.0001
[AB]	—	—	—	—	—	—
Lack of fit	21.20	<0.0001	1.38	0.1702	4.40	<0.0001

AV, acid value, P, porosity; G, gloss; [A], effect of catalyst concentration; [B], effect of pressing time; [AB], effect of the interaction between catalyst concentration and pressing time.

of the effects of the catalyst amount and pressing time on certain technological surface properties of particleboards coated with MF-impregnated decorative papers—chemical resistance (expressed as AV), cleanability (expressed as the porosity), and gloss—are summarized in Table II. The analysis of the effects showed that the two factors tested in the experimental setup had a large influence on the board properties.

For the quantitative modeling of the target values studied, linear models including only the single-factor effects of the catalyst amount and pressing time were used to fit the data (see Table II). The responses were expressed as linear combinations of the significant factors: $AV = -3.81 - 6.42[A] - 0.26[B]$, $P = -1.07 - 5.58[A] - 0.46[B]$, and $G = 351.89 + 311.67[A] + 8.20[B]$, where P is the porosity, G is the gloss, $[A]$ is the amount of the curing

catalyst in the impregnation resin mixture, and $[B]$ is the pressing time. By comparing the magnitudes of the coded factor coefficients, we see that factor $[A]$ is more important than factor $[B]$ for all responses. Considering interaction terms did not lead to significant improvements of the models. For judging the statistical significance of the applied model and of the effects of the analyzed factors, $(P > F)$ was used. $(P > F)$ is the probability of seeing the observed F value if the null hypothesis that there is no factor effect is true. F is calculated by dividing the model mean square by the residual mean square and is used to compare the model variance with residual (error) variance. All linear models showed a very small value for $P > F$ (Table II), and this means that the linear models were statistically significant. The model accuracies for AV and porosity were $R^2 = 0.45$ and $R^2 = 0.37$, respectively, and were thus significantly worse than the one for gloss, $R^2 = 0.95$. The reason for this is that in these cases no continuous scale of measurement values was available. The unsatisfactory accuracy is also reflected by the significant lack of fit observed with AV. Although the robustness and predictive power of the models for AV and P are not very good, however, because both the models and the effects were statistically significant (Table II), the linear models still reflect the actual trends.

On the basis of the linear equations for AV, P, and G based on actual factors, three-dimensional diagrams that directly visualize the effects of the significant parameters were created and are shown in Figure 5(a,b). Figure 5(a) shows the response surface and the corresponding contour line plot from the RSM for P of particleboards coated with MF
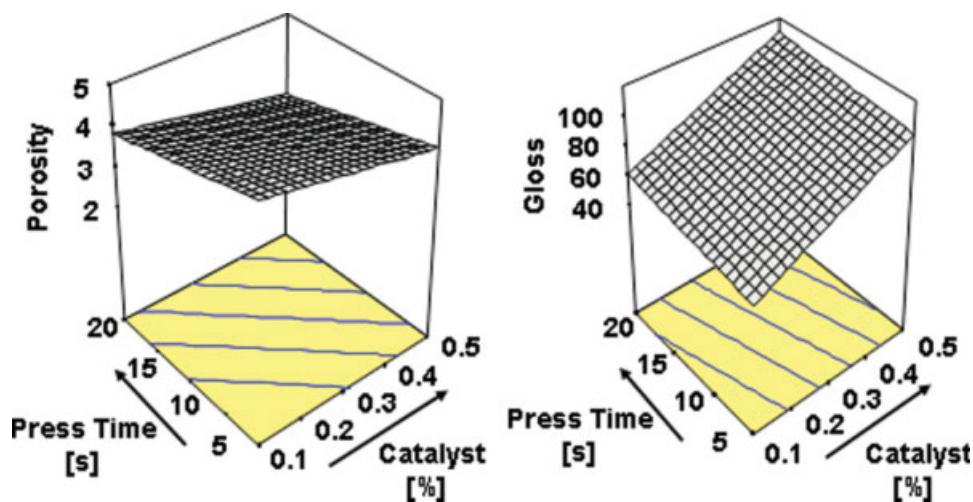

Figure 5 RSM and a corresponding contour line plot for the factor analysis of (a) the porosity and (b) gloss of particleboards laminated with MF-resin-impregnated decorative papers containing different amounts of the curing catalyst and laminated at different press times. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ANOVA Results (Partial Sum of Squares) for the Modified Response Surface Analysis of the Response AV, P, and G Values for Particleboards Coated with an MF-Resin-Impregnated Decorative Paper

	AV		P		G	
	F	$P > F$	F	$P > F$	F	$P > F$
Model	2.32	0.0848	15.16	<0.0001	166.05	<0.0001
[A]	—	—	3.73	0.0639	192.42	<0.0001
[B]	—	—	12.89	0.0013	63.16	<0.0001
[AB]	—	—	—	—	19.78	<0.0001
Lack of fit	—	—	0.20	0.9825	0.42	0.8569

AV, acid value; P, porosity; G, gloss; [A], effect of catalyst concentration; [B], effect of pressing time; [AB], effect of the interaction between catalyst concentration and pressing time.

containing various catalyst levels and laminated for different pressing times. P values for laboratory boards below 3 mean that the surface film quality is sufficiently good and that corresponding industrially manufactured boards will display excellent cleanability. With longer pressing times and higher catalyst percentages, lower values for P and thus better surface quality are obtained, and this indicates that better curing of the resinated paper generally improves board quality. The RSM for AV resembled the porosity (data not shown). Figure 5(b) shows that gloss increases with the pressing time and catalyst amount increasing. In the next step, α, derived from DSC–MFK analysis, was used to supplement the technological dataset, and the RSM was recalculated on the basis of α.

Modified RSM of technological properties

From isoconversional analysis, the degree of MF crosslinking, expressed as α, can be calculated for any pair of reaction time and reaction temperature values. Hence, to each factor level of the pressing time in the experimental design at the pressing temperature of 170°C, a corresponding value of α calculated from an isoconversional analysis of liquid MF can be assigned, and in the RSM, the press time factor can be substituted by the conversion factor. Additional information on the temperature dependence of the responses is thereby introduced into the RSM that was originally derived from data obtained with laminating experiments performed only at 170°C.

Recalculation of the RSM leads to the ANOVA given in Table III. A comparison of Tables II and III reveals significant differences. Although the linear model based on the press time already described AV inadequately, no significant model at all was obtained when the conversion was used instead. Because of the discrete nature of the target value, the arbitrary scale of 1–5 for response value levels was too imprecise for AV, whereas the dataset size and the number of studied factors (2) were too

small. As a result, factor analysis was not satisfactory with this data set. However, increasing the dataset size and the number of factors studied enabled quantitative modeling of AV.[5]

In contrast, with porosity and gloss, significant models can be calculated: $P = +4.06 - 0.44[A] - 1.14[B]$ (for porosity) and $G = +74.41 + 24.17[A] + 26.64[B] - 20.84[AB]$ (for gloss), where [A] is the amount of the curing catalyst in the impregnation resin mixture, [B] is the conversion, and [AB] is the interaction between factor A and factor B. The large $P > F$ values for the lack of fit show that both models are valid and that the corresponding correlation coefficients are at least of the same order of magnitude ($R^2 = 0.95$ for gloss) as or even better ($R^2 = 0.53$ for porosity) than those for the models based on the pressing time.

It is interesting that although the model for porosity is still linear, the relative significance of the factors has changed. When calculated on the basis of the conversion instead of the pressing time, the catalyst concentration becomes the less significant factor, as can be seen from the comparatively low values for $P > F$ and the coded coefficient in the model equation. Moreover, because values for $(P > F) > 0.05$ can generally be considered statistically not significant, it is even justified to discuss the response porosity solely in terms of conversion. The incorporation of α from MFK considerations into the RSM hence leads to a completely new understanding of the system that would not be deducible from one of the methods alone.

In the case of gloss, an additional term was necessary for appropriate data modeling, namely, the interaction term between the catalyst amount and conversion. The meaning of this term becomes immediately clear when the parameter settings of the validation experiments given in Table IV are considered. Because catalysts for MF cure increase the rate of crosslinking directly proportionally to the amount of the catalyst,[5] if the catalyst concentration is raised, a certain degree of conversion will be reached at

TABLE IV
Experimental Settings for the Validation Experiments and Values for the Targeted Porosity and Gloss of the Corresponding Coated Particleboard Surfaces

	Catalyst (%)	Press time (s)	Press temperature (°C)	Conversion (%)[a]	Porosity		Gloss	
					Predicted	Measured	Predicted	Measured
1	0.3	12	165	40	4.2	5.0	72.3	74.7
2	0.4	10	165	40	4.0	4.5	85.0	86.1
3	0.5	8	165	40	3.9	4.0	96.0	97.4
4	0.3	29	165	78	3.3	3.0	84.3	91.8
5	0.4	25	165	78	3.3	3.0	97.7	96.8
6	0.5	21	165	78	3.0	3.5	105.0	101.8
7	0.3	8	175	40	4.2	4.5	78.0	74.7
8	0.4	7	175	40	4.0	3.5	87.3	86.1
9	0.5	5	175	40	3.9	4.5	96.0	97.4
10	0.3	19	175	78	3.3	3.0	85.5	91.8
11	0.4	17	175	78	3.2	3.0	95.7	96.8
12	0.5	14	175	78	3.0	3.0	103.3	101.8

[a] For a specific reaction time and reaction temperature, the corresponding conversion values were determined from MFK–DSC analysis.

shorter pressing times (at fixed pressing temperatures) or at lower pressing temperatures (at fixed pressing times). Hence, in the RSM, the conversion is not an orthogonal factor with respect to the catalyst concentration, and this is reflected by the significant interaction term. In Figure 6(b), the interaction term between the conversion and catalyst percentage leads to the twisted shape of the response surface for gloss.

However, when we consider the small $P > F$ value for [A] in Table III, it is evident that in addition to this obvious interaction with the conversion, the catalyst amount by itself significantly affects surface gloss. This is also illustrated by the plot

depicted in Figure 6(b). When a specific conversion is reached upon lamination, the resulting gloss will be higher with a higher catalyst concentration of the resin mixture. This effect is more pronounced with lower degrees of conversion. According to Figure 6(b), the model predicts a surface gloss close to 100 at conversions as low as 40%, provided that the impregnation mixture contains an appropriately high catalyst amount of around 0.5%. This is rather surprising because it suggests that high gloss does not necessarily require a fully crosslinked resin. In the final step, a set of validation experiments was performed to test the predictions of the modified model.
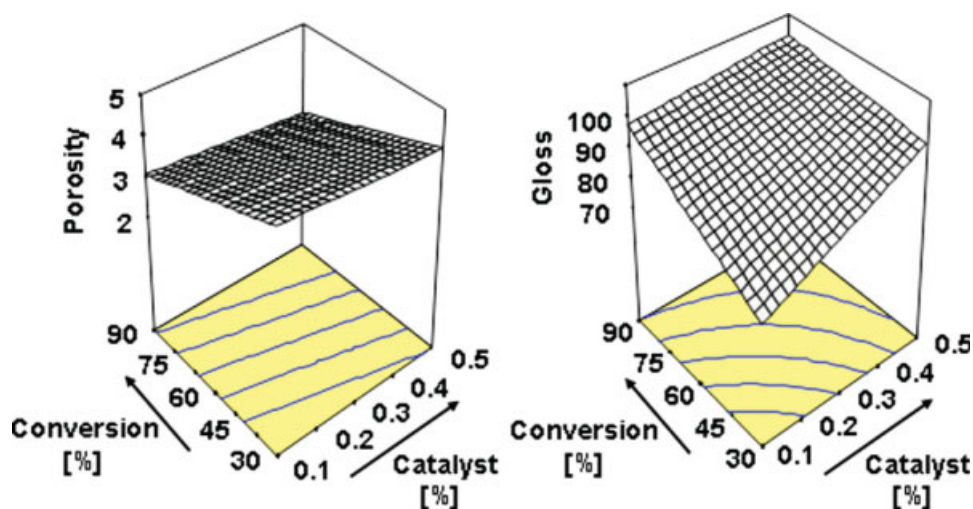

Figure 6 Modified RSM containing input from DSC–MFK and a corresponding contour line plot of the factor analysis for (a) the porosity and (b) gloss of particleboards laminated with MF-resin-impregnated decorative papers containing different amounts of the curing catalyst and laminated at different degrees of conversion. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Validation of modified RSM

To evaluate the applicability of the modified RSM containing information derived from DSC–MFK analysis, a series of validation experiments were performed with pressing temperatures for board lamination that were not used earlier in the derivation of the original RSM. Because in thermal analysis all value pairs of the reaction time and reaction temperature leading to the same values for conversion are treated as equivalent, a specific level of conversion can be obtained by different combinations of the press time and press temperature. The modified model was used to calculate the press times required for either 40 or 78% conversion for different amounts of the curing catalyst in the validation experiments. For example, with the resin containing 0.4% curing catalyst, a pressing time of 10 s was required to achieve a crosslinking degree of 40% at 165°C according to the model, whereas at a temperature of 175°C, only 7 s was required for the same conversion. To validate this equivalence, the validation experiments were performed for selected factor combinations resulting in the same conversion. The parameter settings for the experiments are given in Table IV.

The predictions of the modified RSM and the actual experimental values are summarized in Table IV.

From Table IV, it is evident that the validation samples agreed very well with the predictions of the modified model for both the porosity and surface gloss. No values for AV are discussed because of the lack of model accuracy. With porosity, conversion was predicted to be the major influence, and this was validated by the experiments. Agreement between the calculated and experimental values for porosity was reasonably good. As predicted by the model, experimental settings leading to a high conversion resulted in better surface quality (lower values for P). No significant effect of the catalyst concentration was detected; porosity was exclusively determined by α. As expected from the model parameters, model accuracy in prediction was limited. With gloss (Table IV), only 2 of 12 boards showed significant deviations from the expected values. This illustrates that the model describes reality sufficiently well. It is notable that thermochemical parameters derived from DSC–MFK analysis of liquid resins could be used for modeling the product properties of laminate surfaces.

MF films of equivalent degrees of crosslinking containing the same catalyst concentrations displayed very similar gloss independently of which reaction time/reaction temperature combination was used in pressing. A specific value for surface gloss can be obtained by the use of high press temperatures in combination with short pressing times or vice versa. This means that α reflects the effects of the press program very well. Not surprisingly, higher degrees of conversion give higher values of gloss, as observed earlier when the press time was used as a factor at a fixed temperature. However, boards with the same α value showed even higher gloss with higher catalyst amounts, although this meant that longer pressing times were required. This shows that the catalyst amount influences the surface gloss independently of the absolute degree of crosslinking in the film matrix. Interestingly, the model predicts that high gloss can be achieved even at very low conversions as long as high enough catalyst concentrations are used. This was confirmed by the validation experiments. For example, samples 3 and 9 (high catalyst concentration/low conversion) showed significantly higher gloss than samples 4 and 10 (low catalyst concentration/high conversion). Unlike porosity, gloss does not solely depend on conversion. Hence, the model suggests that the catalyst exhibits a concentration-dependent effect on the reflectivity of the surface film during network formation.

CONCLUSIONS

On the basis of dynamic DSC experiments, $E_a(\alpha)$ and in turn, curing isotherms $[\alpha(t)_T]$ of liquid MF resins were calculated for temperatures relevant to the thermofusion process of decorative laminates in short-cycle presses. The thermochemical information was used to complement a technological dataset for the response surface analysis of two process parameters, the catalyst amount and the pressing time, in laminate manufacturing. When the RSM of the original technological dataset was recalculated on the basis of α derived independently from DSC–MFK analysis, even better RSMs were obtained for porosity and gloss than with the original dataset. Gloss was predicted very well ($R^2 = 0.95$) with the equation for a two-factor interaction model, which was expressed as follows: Gloss = 74.41 + 24.17[Catalyst] + 26.64[Conversion] − 20.84[Catalyst][Conversion]. The incorporation of DSC data into RSM showed that although porosity can be satisfactorily described by conversion only, conversion is not the sole factor influencing surface gloss; the catalyst amount plays a role in the formation of a highly reflective MF surface film. This study demonstrates that MFK parameters derived from an isoconversional kinetic analysis of liquid resins not only are theoretical descriptors but also have direct practical relevance in the modeling of product properties derived from these liquid resins when used to complement technological databases.

References

1. Kandelbauer, A.; Petek, P.; Medved, S.; Pizzi, A.; Teischinger, A. Eur J Wood Prod 2009, 67, to appear.
2. Kandelbauer, A.; Widsten, P. Prog Org Coat, to appear.
3. Kandelbauer, A.; Despres, A.; Pizzi, A.; Taudes, I. J Appl Polym Sci 2007, 106, 2192.
4. Despres, A.; Pizzi, A.; Pasch, H.; Kandelbauer, A. J Appl Polym Sci 2007, 106, 1106.
5. Kandelbauer, A.; Petek, P.; Medved, S.; Pizzi, A.; Teischinger, A. Holz Roh-Werkstoff, submitted.
6. Bauer, K.; Kandelbauer, A. In Proc Nanocoating Days, Aarau; Bachofner, R., Ed.; Sept. 14–15 2004, St. Gallen, Switzerland, p 1.
7. Pizzi, A. Advanced Wood Adhesives Technology; Marcel Dekker: New York, 1994.
8. Mijatowic, J.; Binder, W. H.; Kubel, F.; Kantner, W. Macromol Symp 2002, 181, 373.
9. Vyazovkin, S.; Wight, C. A. Thermochim Acta 1999, 340, 53.
10. Vyazovkin, S.; Wight, C. A. J Phys Chem A 1997, 101, 5653.
11. Bonnet, E.; White, R. L. Thermochim Acta 1998, 311, 81.
12. Saha, B.; Ghoshal, A. K. Thermochim Acta 2006, 451, 27.
13. Adnadevic, B.; Jankovic, B.; Kolar-Anic, L.; Minic, D. Chem Eng J 2007, 130, 11.
14. Sahaa, B.; Ghoshal, A. K. Thermochim Acta 2007, 453, 120.
15. Lopez-Fonseca, R.; Landa, I.; Elizundia, U.; Gutierrez-Ortiz, M. A.; Gonzalez-Velasco, J. R. Chem Eng J 2007, 129, 41.
16. Jankovic, B. Chem Eng J 2008, 139, 128.
17. Vyazovkin, S. In The Handbook of Thermal Analysis & Calorimetry; Brown, M. E.; Gallagher, P. K., Eds.;Elsevier: Amsterdam, 2008; Vol.5, Chapter 13, p 503.
18. Vyazovkin, S.; Sbirrazzuoli, N. Macromol Rapid Commun 2006, 27, 1515.
19. Vyazovkin, S.; Sbirrazzuoli, N. Macromolecules 1996, 29, 1867.
20. Sbirrazzuoli, N.; Vyazovkin, S. Thermochim Acta 2002, 388, 289.
21. Liu, W.; Qiu, Q.; Wang, J.; Huo, Z.; Sun, H. Polymer 2008, 49, 4399.
22. Alonso, M. V.; Oliet, M.; García, J.; Rogríguez, F.; Echeverría, J. Chem Eng J 2006, 122, 159.
23. Wang, J.; Laborie, M.-P. G.; Wolcott, M. P. Thermochim Acta 2005, 439, 68.
24. Kandelbauer, A.; Wuzella, G.; Mahendran, A.; Taudes, I.; Widsten, P. Chem Eng J, submitted.
25. Vyazovkin, S. J Comp Chem 2001, 22, 178.
26. Ferg, E. E.; Pizzi, A.; Levendis, D. J Appl Polym Sci 1993, 50, 907.
27. Mercer, A. T.; Pizzi, A. J Appl Polym Sci 1996, 61, 1687.
28. Mercer, A. T.; Pizzi, A. J Appl Polym Sci 1996, 61, 1697.
29. Vyazovkin, S. J.; Dollimore, D. J Chem Inf Comput Sci 1996, 36, 42.
30. Flynn, J. H.; Wall, L. A. J Res Nat Bur Stand A 1966, 70, 487.
31. Ozawa, T. Bull Chem Soc Jpn 1965, 38, 1881.
32. Kissinger, H. E. Anal Chem 1957, 29, 1702.
33. Akahira, T.; Sunose, T. Res Rep Chiba Inst Technol (Sci Technol) 1971, 16, 22.
34. Budrugeac, P.; Segal, E. Int J Chem Kinet 2001, 33, 564.
35. Vyazovkin, S. Int J Chem Kinet 2002, 34, 418.
36. Bronstein, I. N.; Semendjajew, K. A. Taschenbuch der Mathematik; Verlag Harri Deutsch: Frankfurt, Germany, 1993.
37. Doyle, C. D. J Appl Polym Sci 1962, 6, 639.
38. Coats, A. W.; Redfern, J. P. Nature 1964, 201, 68.
39. Gorbachev, V. M. J Therm Anal Calorim 1975, 8, 349.
40. Agrawal, R. K.; Sivasubramanian, M. S. J Am Chem Eng 1987, 33, 1212.
41. Cai, J.; Yao, F.; Yi, W.; He, F. J Am Chem Eng 2006, 52, 1554.
42. Vyazovkin, S. Int J Chem Kinet 1996, 28, 95.
43. Petek, P.; Böttcher, A.; Kandelbauer, A. In Conference Proceedings of the European Laminates Conference and Workshop; Fischer, K., Ed.; April 4–6 2006, Prague, Czech Republic, Paper 7: p 1.
44. Myers, R. H.; Montgomery, D. C. Response Surface Methodology; Wiley: New York, 2002.