Received: 9 October 2020 | Revised: 2 February 2021 | Accepted: 6 February 2021

DOI: 10.1002/app.50635

ARTICLE

Applied Polymer SCIENCE WILEY

Multivariate process trajectories for molecular description of MF thermal curing and correlation with hydrolytic stability

Stephanie Weiss[1] | **Regina Seidl**[1] | **Waltraud Kessler**[2] | **Rudolf W. Kessler**[2] | **Edith M. Zikulnig-Rusch**[1] | **Andreas Kandelbauer**[3]

[1]Wood K plus- Kompetenzzentrum Holz GmbH, Veit an der Glan, Austria

[2]Kessler ProData GmbH, Reutlingen, Germany

[3]Lehr- und Forschungszentrum Process Analysis and Technology (LFZ PA&T), School of Applied Chemistry, Reutlingen University, Reutlingen, Germany

Correspondence
Andreas Kandelbauer, Reutlingen University: Hochschule Reutlingen, Alteburgstrasse 150, Reutlingen, Baden-Württemberg 72762, Germany.
Email: andreas.kandelbauer@reutlingen-university.de

Funding information
Austrian Research Promotion Agency (Österreichische Forschungsförderungsgesellschaft) FFG, Grant/Award Number: COMET Wood 865 905

Abstract

During curing of thermosetting resins the technologically relevant properties of binders and coatings develop. However, curing is difficult to monitor due to the multitude of chemical and physical processes taking place. Precise prediction of specific technological properties based on molecular properties is very difficult. In this study, the potential of principal component analysis (PCA) and principal component regression (PCR) in the analysis of Fourier transform infrared (FTIR) spectra is demonstrated using the example of melamine-formaldehyde (MF) resin curing in solid state. FTIR/PCA-based reaction trajectories are used to visualize the influence of temperature on isothermal cure. An FTIR/PCR model for predicting the hydrolysis resistance of cured MF resin from their spectral fingerprints is presented which illustrates the advantages of FTIR/PCR compared to the combination differential scanning calorimetry/isoconversional kinetic analysis. The presented methodology is transferable to the curing reactions of any thermosetting resin and can be applied to model other technologically relevant final properties as well.

KEYWORDS

coatings, crosslinking, resins, spectroscopy, thermosets

1 | INTRODUCTION

Industrial processes and manufacturing are currently subject to considerable change to meet future demands due to increasing competition, globalization, cost pressure, quality assurance, and mass customization of the final products. Manufacturers need to meet increasingly demanding quality requirements of pre-pregs and final products. Therefore, the process parameters during production have to be optimized.[1] The process analytical technology (PAT) and quality by design (QbD) platform of the US Food and Drug Administration (FDA) or the initiative for the fourth industrial revolution "Industry 4.0" in Germany as well as the US Industrial Internet of Things (IIoT) have raised the awareness that process understanding, knowledge-based production and the development of process control strategies is of great importance to assure quality control, product safety, and production efficiency.[2–4] In this context, intelligent production and process understanding on a molecular and mechanistic level is a key issue.[4]

To address the processing of thermosetting materials with PAT strategies on a molecular level throughout the various production steps is very demanding. In contrast to thermoplastics, the actual polymer skeleton of

thermosets is built up only during processing to the final product from pre-polymers. This makes it difficult to follow the production of the polymer with analytical methods, since the actual "synthesis" of the material until 100% conversion is reached is ultimately distributed across a wide range of manufacturing processes. Therefore, the understanding of structure–property relationships in thermosets is automatically closely linked to the process-analytical monitoring of the polymerization during the manufacturing process and especially during the final curing.

MF resins are widely used in the wood-based panel industry as adhesives and as surface coatings for decorative laminates. In the latter case, décor paper is coated with MF resins and further glued onto a carrier material in a hot press.[5–7] MF resins exhibit outstanding resistance against hydrolysis, various chemicals (such as solvents, acids and bases, and hot water) and high temperature (thermal stability up to at least 180°C) as estimated by steam resistance tests. To provide protection, the surface of the final product should be uniformly coated without defects due to incomplete curing of the applied MF resin film.[1,7] If the curing is not carried out under ideal conditions and tailored to the respective desired product properties as well as further processing requirements, further processing of the produced laminates, for example, sawing, drilling can lead to damages of the surface and the application properties may suffer.[8] Furthermore, the optical appearance is important as well.[7] Hence, appropriate process design based on PAT strategies is important to tailor product performance.

Thermosetting resins like MF are especially difficult to address analytically due to the low solubility in the cured state. Furthermore, the complex condensation reaction and a rapid change in morphology with progression of the ongoing cross-linking reaction presents an analytical challenge.[9–11] Analytical methods that provide sufficient sensitivity and selectivity for optimization and quality control are therefore needed. In process control strategies, usually only sum parameters like temperature–time diagram or pressure are measured and controlled. However, these data are only indirectly connected to the actual target responses of interest like, for example, hydrolytic stability of the coating.[3,12] In polymer analytics, thermo analytical methods like differential scanning calorimetry (DSC), are widely used to predict the behavior of the polymer during manufacturing.[1,13–17] Again, a sum parameter (enthalpy changes) is measured. However, in the context of implementing strategies of "Industry 4.0" or IIoT, thermo analytical methods have limited applicability, as online or inline analysis is not possible. Furthermore, sample size and obtaining representative samples from a whole production line lead to further difficulties.

In contrast, optical spectroscopy provides important quality parameters on a molecular level, like the chemical composition of the mixture, gives insights on structural properties on a submicroscopic and nanoscopic scale or yields even information about polymer particle size distribution.[18,19] Furthermore, spectroscopic methods have a high potential for real-time online and inline installations in production processes in the context of PAT and IIoT. However, due to the complexity of the obtained spectra, further chemometric processing of the data is often needed to extract useful information from the complex spectral patterns. By applying multivariate data analysis (MVA) the spectral information can be related to quality attributes of the desired products.[3]

In the present study, the curing of MF resins is investigated as a representative example for a complicated curing reaction using Fourier transform infrared (FTIR) spectroscopy in combination with chemometric tools. The aim of the study is to apply concepts of PAT to improve the understanding of the curing reaction of MF resins to monitor, support and control production processes in the future. To retrieve information during the reaction on a molecular basis, real-time FTIR spectra were recorded during network formation. The spectral progression during cross-linking was then correlated with an important resin quality parameter, the resistance against acidic hydrolysis. In order to exploit the complex information inherently present in the IR spectra, in addition to classical peak assignment the chemometric tools principal component analysis (PCA) and principal component regression (PCR) were applied. PCA is used to reduce the dimensionality of the multidimensional space of spectroscopic information into a few principal components (PCs) often also called "latent variables." The scores of the measurements can be used as multivariate process trajectories similar to, for example, a univariate conversion degree from DSC-measurements. The scores are calculated from spectra, which means they contain molecular chemical information. In a first step, the obtained scores and loadings plots are explained and discussed separately. Thereafter, the scores and loadings results are interpreted together and the obtained reaction trajectories are visualized over time. Finally, an application property like hydrolytic stability can be predicted and interpreted on a molecular level using the PCR methodology.

2 | MATERIALS AND METHODS

2.1 | Chemicals and reagents

Melamine formaldehyde resin (trade name: Kauramin 773, M:F = 1.6 = 0.62) was obtained as a spray-dried powder from BASF (Ludwigshafen, Germany). The powder was used directly for the measurements and preparations.

2.2 | IR spectroscopy

ATR-FTIR spectroscopy measurements were performed on a Bruker Tensor 27 with a "Golden Gate Heated Diamond Top Plate" using the OPUS 2.7 software package. MF pre-polymer powder was placed on top of the plate at the given temperature and the temperature was kept constant during recording of the spectra. Measurements were done twice for each parameter setting and then averaged. Spectra were recorded every minute in the range from 4000 to 600 cm^{-1} versus air as the background spectrum with a resolution of 4 cm^{-1} and a scan rate of 32 scans per spectrum. The curing reaction was monitored isothermally at 100, 120, 140, 160, and 180°C for 40 min.

2.3 | Multivariate data analysis

MVA of the IR spectra was performed using the Unscrambler X 10.4 software package (CAMO Software AS, Oslo, Norway). Two spectral ranges were analyzed separately: (1) the fingerprint region from about 1670–700 cm^{-1} and (2) the region from 3500 to 2800 cm^{-1}. Two single acquired spectra were averaged and unit vector normalization was applied to the resulting mean spectra. PCA was performed with the mean centered, normalized spectra. The PCs were determined using the NIPALS-algorithm.

PCR was used to quantitatively describe the relationship between the IR spectra and the hydrolytic stability of differently cured resin samples. The models were built using the normalized IR spectra from mean centered data as input x-variables. The response y-variable was hydrolytic stability. PCR uses a standard multilinear regression algorithm. For PCR, a randomly segmented cross validation using five segments was carried out. The results are reported as root mean square error of cross validation (RMSECV).

2.4 | Hydrolysis testing

MF pre-polymer powder was transferred into an aluminum cup and cured at 100, 120, 140, 160, and 180°C in a drying oven for 7 min. Afterwards, the brittle solids were ground to a fine powder. About 400 mg of the differently cured resin samples were weighed into a 100 ml volumetric flask and dist. Water and 1 ml conc. HCl were added. Afterwards, the flask was filled to a defined volume (100 ml) with distilled water. The solution was mixed thoroughly and left to react for 48 h. The free formaldehyde content in the aqueous solutions was then determined photometrically based on the Hantzsch' reaction with acetylacetone.[20,21] For this, the solutions were filtered to remove solids present. To 1 ml of the obtained clear solution, 5 ml of dist. Water and 4 ml of the acetylaceton-reagent were added. After 2 h, the absorbance of the solution was measured at 412 nm. The standard error SE of the free formaldehyde determination is ±0.23 weight %.

2.5 | DSC measurements

The thermograms were recorded using a differential scanning calorimeter DSC 822^e by Mettler Toledo. For each measurement, about 5 mg of MF resin were weighed into a high-pressure gold coated stainless steel crucible (30 µl) which was sealed and subjected to a temperature gradient ranging from 25 to 250°C with five different heating rates (2, 5, 10, 15, and 20°C min^{-1}). The enthalpy changes were recorded and analyzed using the STARe 15.00a software package. The results of the DSC experiments were further used for iso-conversional kinetic analysis. Conversion degree dependent activation energy profiles were determined from the five runs at different heating rates using the advanced form of the Vyazovkin method.[22,23] These profiles were then used for calculation of the theoretical isotherms. Validation was performed by a combination of dynamic and isothermal measurements.

3 | RESULTS AND DISCUSSION

3.1 | IR spectra and band assignment

The curing reaction of MF resin was monitored in real-time by ATR-FTIR measurements. The resin was cured under isothermal conditions at different temperatures. In a previous study,[24] a detailed band assignment of the present resin system was performed at different curing degrees by static FTIR measurements. The former study[24] showed that IR spectra can reveal useful information when using the fingerprint region of the IR spectra. Thus, in the following section, the focus is given to the spectral region between 1670 and 700 cm^{-1}. Only the most important changes in the spectra are discussed. For a more detailed band analysis the former study[24] is recommended. Exemplary for all measurements, the characteristic spectral changes during the network formation are displayed for the experiment at 140°C (see Figure 1).

Melamine formaldehyde resins show two characteristic bands of the triazine ring. One sharp band at about 810 cm^{-1} and one band at around 1540 cm^{-1} which overlaps strongly with the region of the C—H absorption bands. These triazine ring bands do not change significantly during curing. At about 1620 cm^{-1}, primary amine

vibrations are present that decrease during curing due to the formation of bridged species. In the region of 1500 to about 1400 cm^{-1}, several C—H absorption bands of CH_2 groups are present. The position of the C—H vibrations changes during the reaction since the ratio of methylol, methylene, and methylene-ether groups changes during condensation. A shift of the strong X-sensitive C_{Ar}-N absorption band in the region of 1350–1315 cm^{-1} is clearly visible. As this band is affected by the nature of the substituent at the amine function, this shift indicates the formation of either methylene ether or methylene bridges and hence an increase of cross-links during condensation. In addition, the conversion of methylol moieties during cross-linking is seen by the decreasing absorbance at about 990 cm^{-1} representing the C—O stretch of primary alcohols. Simultaneously, bands attributed to the C—O—C vibrations of methylene ether moieties at about 1030 cm^{-1} and in the area of 1140 cm^{-1} increase with increasing reaction time and temperature due to the formation of methylene-ether bridges. However, this region overlaps with other C—N vibrations as well.[24,25]

3.2 | Univariate analysis of MF cure based on single absorbance peaks

Cure monitoring and determination of the conversion degree is usually done in a univariate way, that is, by following the absorption intensity of a single characteristic band in the spectrum.[16] Typically, either the decreasing or increasing absorbance at a single wavelength or the respective peak integral is used as the univariate information. As every absorption band carries chemical information on a molecular level, mechanistic insights on how the functional groups react with each other can be concluded.

Bands suitable for univariate analysis must meet the following criteria:

a. Unambiguous assignment to a functional group of interest.
b. No overlap with other bands.
c. High-peak intensity.
d. Generally, a good signal to noise ratio of the recorded spectra.

These criteria are generally not easy to meet, especially in the fingerprint region of the IR spectrum. With some reactions, conversion course can readily be followed spectroscopically as in the case of PU systems due to the characteristic isocyanate band,[26] certain photo-induced reactions like the network formation of thiol-ene or thiol-acrylate systems[27] or epoxy resins.[16]

In the case of MF resins, the bands of the C—O and C—N vibrations can in principle be used for univariate monitoring of the cross-linking reaction. This was, for example, done for the synthesis and the end-point detection of MF resins.[28] For the normalized IR data, the decrease of the methylol-function at about 1000 cm^{-1}, the increase of the band at about 1160 cm^{-1} and the band at 1336 cm^{-1} from the resulting band shift were used to calculate conversion functions over time. Exemplarily, the experiments at 140 and 160°C are compared with each other. Figure 2 shows the courses of conversion of the three bands for these experiments. It can be seen very clearly that, depending on the wavelength used for univariate evaluation, very different kinetic profiles are obtained in detail for the curing process. Different chemical functions are transformed on different time scales and to varying extent. A single definitive conversion curve that is representative for the whole system can therefore not be derived based on only one single arbitrarily selected wavelength. Evaluated together, however, this information can provide a deeper insight into the curing reaction.

Monitoring the overall MF curing reaction based on univariate analysis, generally, is prone to several problems. None of the bands meets the required criteria mentioned above exactly. Information from one band might be also present in the signal of a neighboring vibration to a certain extent making deconvolution of the bands difficult. In addition, a complete turnover for the last spectrum is assumed to have taken place for all bands. However, different chemical functionalities can react to different (and unknown!) degrees.

The value of information derived from univariate analysis of the IR spectra is thus limited, since only the

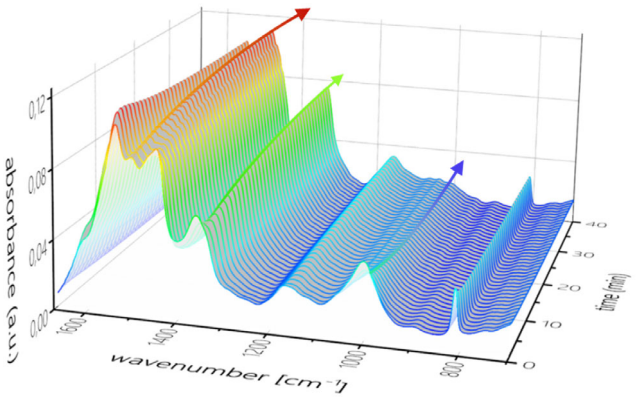


FIGURE 1 Normalized FTIR spectra from 1670 to 700 cm^{-1} of MF resin cure at 140°C over a time period of 40 min. FTIR, Fourier transform infrared [Color figure can be viewed at wileyonlinelibrary.com]

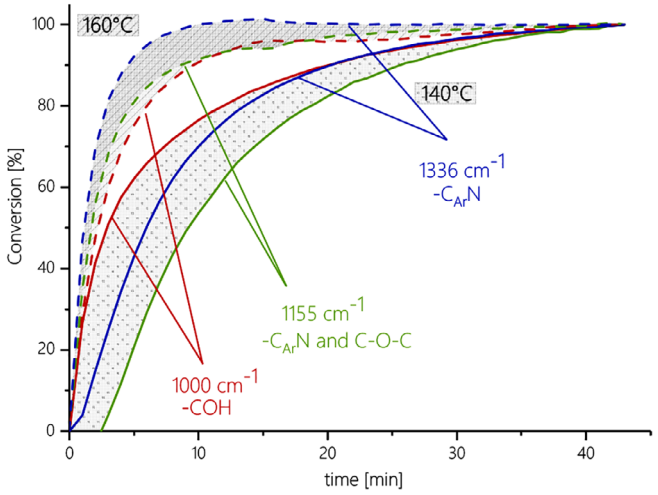


FIGURE 2 Conversion degree functions at 140 and 160°C determined by following the absorption of single IR peaks [Color figure can be viewed at wileyonlinelibrary.com]

consumption or formation of single functional groups are monitored. No conclusions on network density or network type can be deduced, since although related, the group specific information is not completely equivalent to such complex information.

3.3 | Multivariate analysis of MF cure based on PCs and multivariate process trajectories

3.3.1 | PCA and process trajectories

The chemometric analysis of the FTIR spectra obtained during MF resin cure in real-time was performed by PCA. PCA belongs to the toolbox of MVA methodologies. The intention of PCA is the reduction of dimensionality of the original data. Data reduction proceeds by combining variables, which contain correlated information. In this way, a large number of variables, in our application the absorbance values at different spectral wavenumbers, can be reduced to a much lower number of so-called PCs (latent or "hidden," underlying variables). Variables that do not change significantly within the sample set are considered to be less important than variables with a high variance within the samples.[10,29] Mathematically, different methods for the calculation of the PCs can be applied. The PCs are independent from each other (orthogonal) and form a new coordinate system, which contains the relevant information regarding the investigated samples and substitutes the original multidimensional coordinate system. The original spectra are represented in this new PC coordinate system as linear combination of the different PCs weighted according to the impact of this PC to the spectra. The weightings for each PC in the linear combination of the reproduced spectra in the data set are called scores. The weightings for the variables in the PCs are called loadings. The higher the explained variance by a PC, the higher is the contribution of this PC to the total variance of the system.[29]

MVA provides thus several advantages compared to a simple univariate approach and enables analyzing a highly multidimensional data set in only a few dimensions. By using all spectral variables simultaneously, correlated information can be withdrawn from the data set that would not be available when analyzing the individual variables separately. In the case of IR spectra, even small changes that might not be clearly visible using a univariate approach can be taken into account. Hence, shoulders of bands or other small bands are also recognized and included in the analysis. This is for example important for reaction kinetics to determine the reaction pathway or reaction trajectory calculated from the spectra over reaction time when similar components are produced like in resin chemistry. In that way, different resin systems or catalysts can be compared with each other.[29,30]

In general, the concept of multivariate process trajectories can be a helpful tool for process analysis. Process trajectories visualize a series of measurements during the process within an analytical space. The selected variables can be physical (e.g., temperature or pressure) or virtual variables, the latter coming from mathematical transformations like chemometric calculations (e.g., PCs from PCA) as described before. These trajectories are useful to support real-time process analysis, process monitoring and control, increase the process understanding and are used to further optimize production processes.[12]

3.3.2 | Scores plots: Kinetic description of the cure reaction using PCA process trajectories

Compared to the univariate approach, using MVA allows to take the complete chemical information of the chosen spectral area into account. The chemical information is accessible via the loadings plots, the reaction course is described in the score data space over time. All experiments can be analyzed together statistically, a direct comparison of the process trajectories is then possible. No preliminary assumptions regarding conversion degree must be made.

Three PCs (PCs) are sufficient to describe the data set as they cover 99% of the spectral variance of the data. From the scores plot versus time, it can be seen, how far the reaction has progressed and which chemical state has been reached at a certain point of time. Figure 3(a)–(d)

shows the evolution and progress of the score value of the individual PCs with time. Score values in this case can be treated like concentration changes of chemical components over time and represent the process trajectory of an ongoing reaction. These two-dimensional process trajectories are related to the chemical functionalities of the polymer. In the case of MF resins these are basically methylol entities, methylene-ether bridges or methylene-bridges, just to name the most important ones.

Usually, for PCA of spectroscopic data mean centered data are used to enhance the variability around the average spectrum. Therefore, the mean spectrum has the score value zero. Positive and negative score values then represent deviations of the individual spectra from this mean.

Figure 3 shows that with higher temperature the PC 2 (red) decreases markedly with time. The time course follows the typical course of a reactant that is consumed. PC 2 can therefore essentially be assigned to those functionalities whose concentrations gradually decreases during the curing process. In the case of MF resin, these are methylol functionalities. However, this does not mean that PC 2 can be identified exactly with "the" methylol. It rather means that the essential information contained in PC 2 is closely related to methylols. From the literature, it is known that at lower temperatures a comparatively low degree of cross-linking is achieved. This means that the relative amount of methylol functionalities must be larger than at higher temperatures.[9] This pattern is seen in the scores plot for PC 2 in Figure 3.

The scores of PC 1 (blue), on the other hand, increase over time, that is, the chemical functionalities whose spectral fingerprint is reflected by this principle component is formed during the curing process. The score values of PC1 increase especially at the intermediate temperatures 140 and 160°C (Figure 3(b),(c)). At very low (120°C) and very high (180°C) temperatures, on the other hand, only negative score values are visible (Figure 3(a), (d)). This pattern fits the formation of ether bridges: During curing, methylene ether bridges and methylene bridges are formed. At high temperatures, methylene bridges predominate, at moderate temperatures ether bridges are

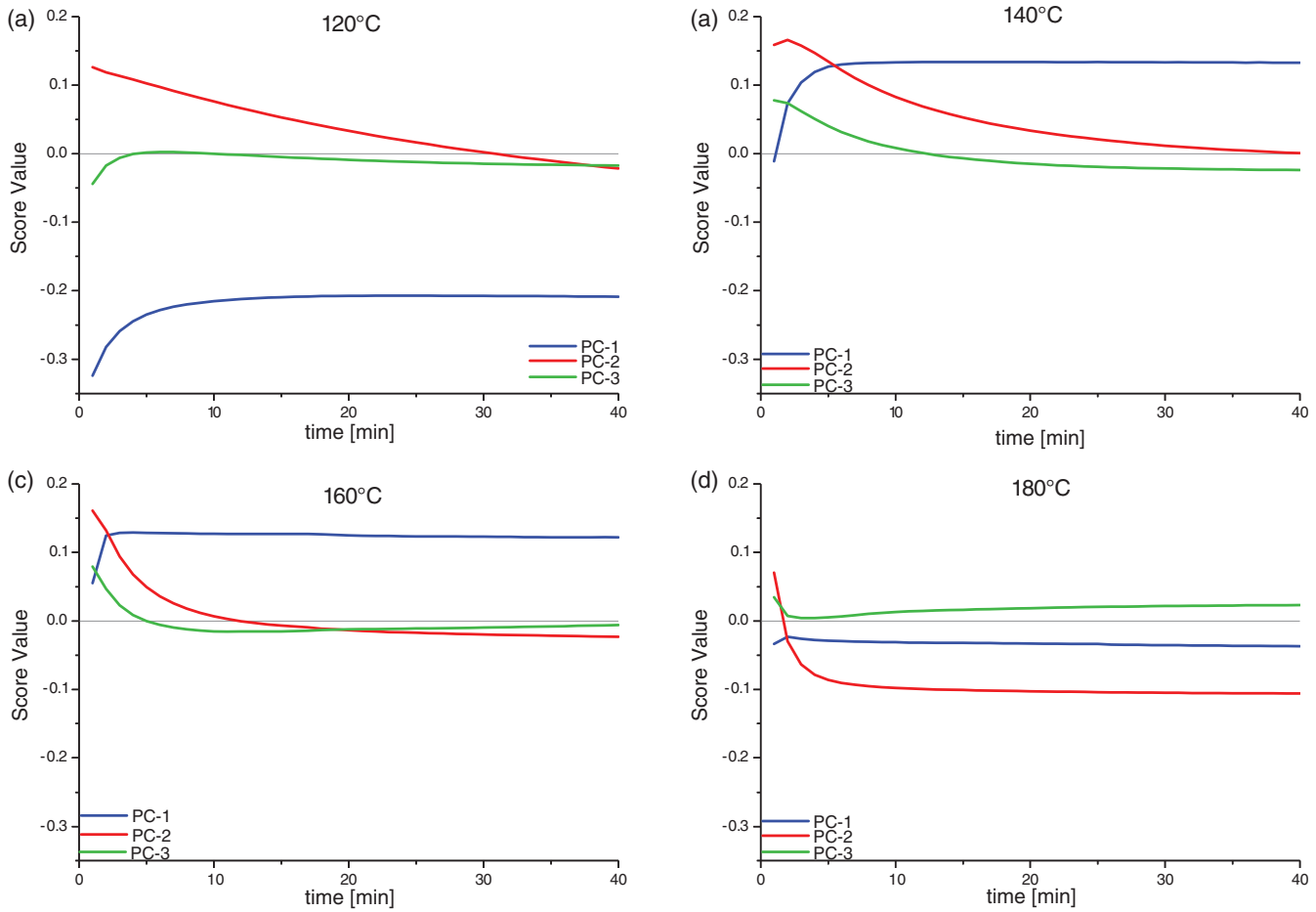


FIGURE 3 Score values of the three principal components as process trajectories of the ongoing curing reaction with time at (a) 120°C, (b) 140°C, (c) 160°C, and (d) 180°C [Color figure can be viewed at wileyonlinelibrary.com]

more likely to form. At low temperatures there is little overall cross-linking.[9,31]

Assuming that MF resins consist essentially of building blocks with the three chemical functionalities methylol, ether bridges and methylene bridges, then PC3 can only be assigned to structural elements, that are characterized predominantly by methylene bridges. This agrees particularly well with the strong increase of PC3 scores at 180°C. Here, only PC3 shows positive score values.

This interpretation is only a rough estimation, not an exact identification. Principle Components do not only contain the information of single functional group vibrations, but of the entire information over the whole spectral range and condense this information into single score values. Therefore, these score values are always influenced by other effects (peak shifts, morphological changes, etc.) as well. It can be assumed, that in complex polymeric systems like MF resins, all three of the different types of chemical entities are simultaneously present. The relative proportions differ significantly depending on the reaction conditions. As curing progresses, these proportions change with conversion.

In order to support this rough classification with specific information from IR data, the loadings are briefly discussed below.

3.3.3 | Loadings plots: Attempt to interpret the molecular structure of the network components

Figure 4 shows the resulting three PCA loadings plots obtained by the PCA of all measured spectra within the temperature range from 120 to 180°C. The PCs are purely mathematical entities, which combine several correlated variables, thus the physical or chemical interpretation of the PCs is not always straightforward.[12] However, in a structured dataset where variation is systematically introduced by designed experiments, the meaning of the PCs may be deduced and annotated to corresponding variations in the experimental factors. In this case, these peaks can be treated like an infrared spectrum, although there are positive and negative peaks visible.

In general, the higher the contribution of a single wavenumber to the total variance of the PC, the higher is the absolute loadings-value. The plus or minus sign gives the direction of the correlation between the variables.[10] As the spectra are mean centered before PCA, the 0-level of the scores- and loadings plots is thus the mean of all spectral features. Positive loadings values combined with positive scores values mean, that the absorbance values in the original infrared spectra are above average at this wavelength. The same applies for negative loadings combined with negative scores values. In this combination of scores and loadings the original infrared absorbance spectra show also above average absorbance intensities.

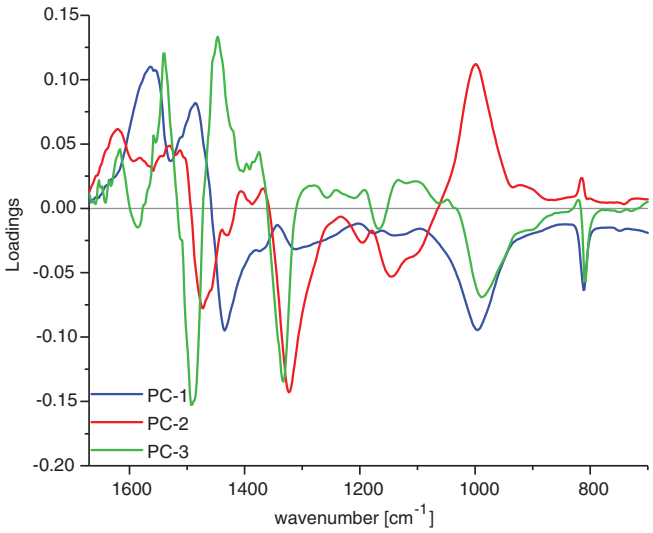


FIGURE 4 PCA loading plots of PC-1, PC2, and PC-3 of IR spectra during the cross-linking reaction of MF resin at 120, 140, 160, and 180°C. PCA was performed using all spectra recorded at all studied temperatures. PCA, principal component analysis [Color figure can be viewed at wileyonlinelibrary.com]

The loadings plots for PC2 and PC3, unlike PC1, can be attributed straight forward to the dominant features in the area of methylol bands (C—O vibration at 1000 cm^{-1}) and to strong differences in the area of the —CH_2 bands in the range between 1500 and 1400 cm^{-1}. The methylol moieties at 1000 cm^{-1} disappear clearly during the curing reaction as a strong positive or negative loading value is present in this region. This goes hand in hand with the decrease of bands in the area of 1620 cm^{-1}, which can be assigned to primary amine functions and water. At the same time, an increase of the band at about 1325 cm^{-1} is observed. This band has negative loading values as this band results from the peak shift of the C_{Ar}-N band during the network formation. The region between 1200 and 1060 cm^{-1} increases together with the peak at 1325 cm^{-1} and can be assigned to C—N bands and methylene ether bridges. In the range from 1500 to 1400 cm^{-1} various CH_2 bands absorb which are hardly distinguishable from each other. As the band at 1475 cm^{-1} shows the same trend as the band at 1325 cm^{-1} in the loadings-plot, this region could be derived from CH_2 groups of methylene bridges or methylene-ether bridges. When the knowledge of the kinetic evolution of the scores is also included, an assignment to different functional groups can be made. PC2 (12% of the overall spectral information) thus represents the decrease of methylol moieties during the cure reaction and PC3 (4%) is more related to the formation of

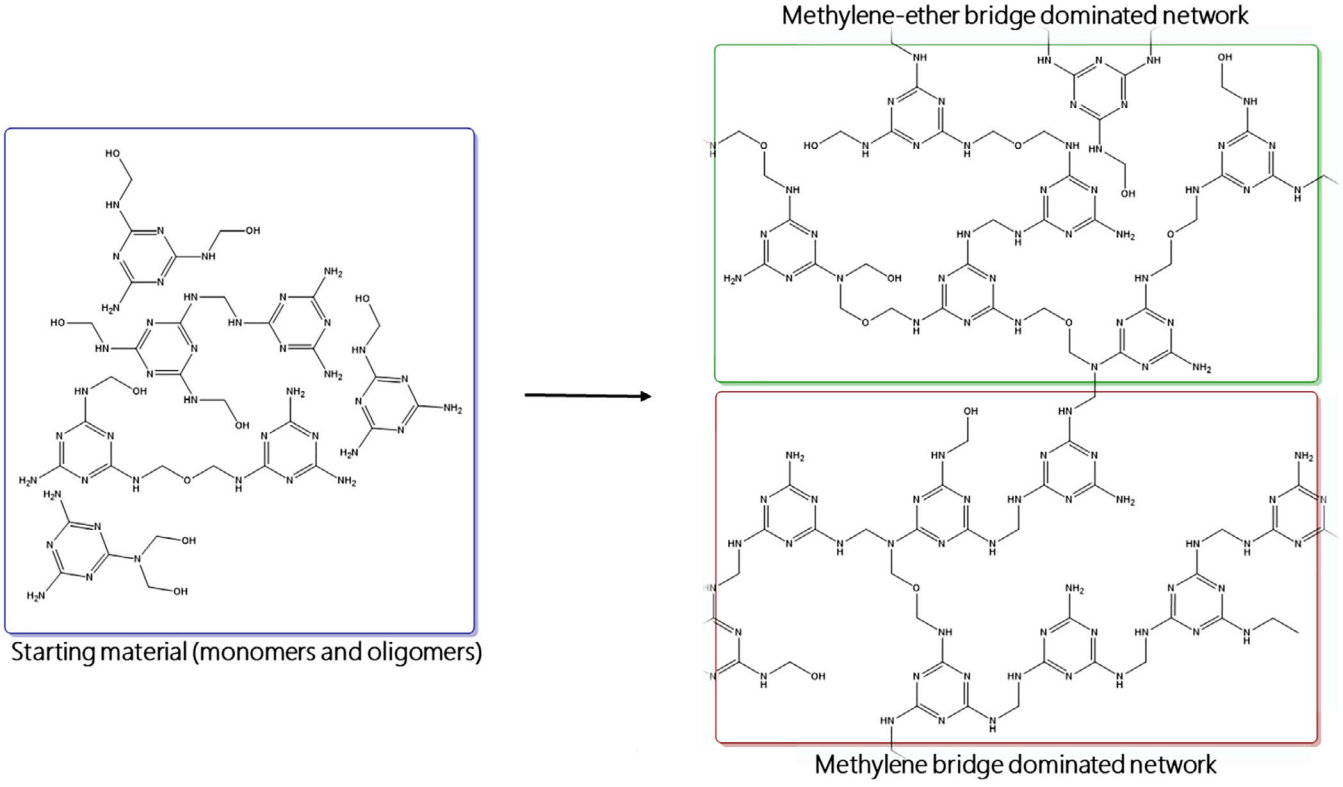
the methylene dominated network formed at higher temperatures.

PC1 contributes to about 83% of the overall spectral features, but is more difficult to attribute to a single moiety than PC2 or PC3. PC1 represents the highest variations within the spectral features and can be related to the influence of the curing temperature by the selection of the isothermal curing temperature. This includes various chemical and structural changes taking place during the curing reaction such as increased cross-linking, viscosity and brittleness of the resin that lead to changes in the photonic scattering behavior.[32] For example, at 140 and 160°C, the resin samples form a transparent resin film, whereas at 120°C the samples still have a powdery structure and at 180°C, the sample is already very brittle even after short reaction times. These complex general differences between the samples are extracted from the data set and summarized in PC1. From a chemical point of view, it is plausible to assign the spectral features of the loadings to the -contribution of methylene-ether-moieties.

Scheme 1 depicts the chemical structures of the starting materials (monomers and oligomers, Scheme 1, left) involved in MF resins and a simplified structural representation of the most important functional groups present cross-linked MF network structures (Scheme 1 right). The cross-linked MF network structure is intended to illustrate the basic types of functional groups present in MF materials and cannot reflect the actual complexity present in real resin. The various types of functional groups and chemical linkages depicted in Scheme 1(b) are present in varying amounts at any stage of resin curing and contribute to various extents to the spectral features of the MF network at any moment.

3.3.4 | Influence of temperature on reaction course: Multidimensional process trajectories

The results of the PCA clearly show the reduction of the spectral information from a multidimensional space to a low-dimensional space that is built from the calculated three principle components. However, it is difficult to develop an understanding of the curing process as long as the individual principle components are considered separately. Figure 5(a) shows the reaction trajectories in the PC1-PC2-PC3-domain. In Figure 5(b) the reaction course over time in the PC1-PC2-dimension, in Figure 5 (c) the PC2-PC3-dimension over time and in Figure 5(d)



SCHEME 1 Monomeric and oligomeric building blocks present in MF resin (left side) and schematic representation of the most important functional groups and the two types of chemical linkages (methylene-ether and methylene bridges) present to varying amounts in MF network at any time during the curing process. MF, melamine-formaldehyde [Color figure can be viewed at wileyonlinelibrary.com]

the PC1-PC3-dimension over time of the curing reaction is shown.

Every point in a trajectory represents one spectroscopic measurement. In the three-dimensional plots shown in Figure 5, the time sequence of individual measurements is translated into a spatial sequence. This means that points that are close together in this plot represent spectra that show only small differences to each other. Thus, they describe states of the resin that change only slightly within the time interval between two measurements. Points that are far apart from each other in this plot thus indicate that the corresponding molecular state of the resin has changed very strongly during the transition from one measurement to the next. A sequence of distant points thus describes a fast process, while a sequence of closely spaced points corresponds to a slow process. The direction in which a certain sequence of points develops in the 3D plots in Figure 5 indicates in relation to which PC the structural properties of the resin change from one measurement to the next. Thus, after assigning the PC to a real property, the reaction trajectory can be used to describe which inherent properties of the system change accordingly.

The reaction spectra were measured every minute during cure. It can be seen in Figure 5 that especially in the initial phase of hardening, the individual points in the 3D plot are very far apart. In contrast, the points at the end of the reaction trajectory are generally much closer together. As the reaction progresses, the distance between the points gradually decreases. This means that the curing process is much faster at the beginning and slower toward the end.

Figure 5(b) shows that the temperature has a very large influence on the reaction speed. The higher the temperature, the faster the reaction. Curing, which was carried out at 180°C, is very fast and comes to a virtual standstill within 5 minutes. The changes take place mainly in the direction of PC 2, along the PC 1 axis the point does not shift at all. Figure 5(b) shows no further changes in the direction of PC 1 or PC 2 after 5 min. The reaction trajectory moves through the score space only along the time axis. Figure 5(c) shows, however, that not all chemical reactions have come to a complete standstill after 5 min.

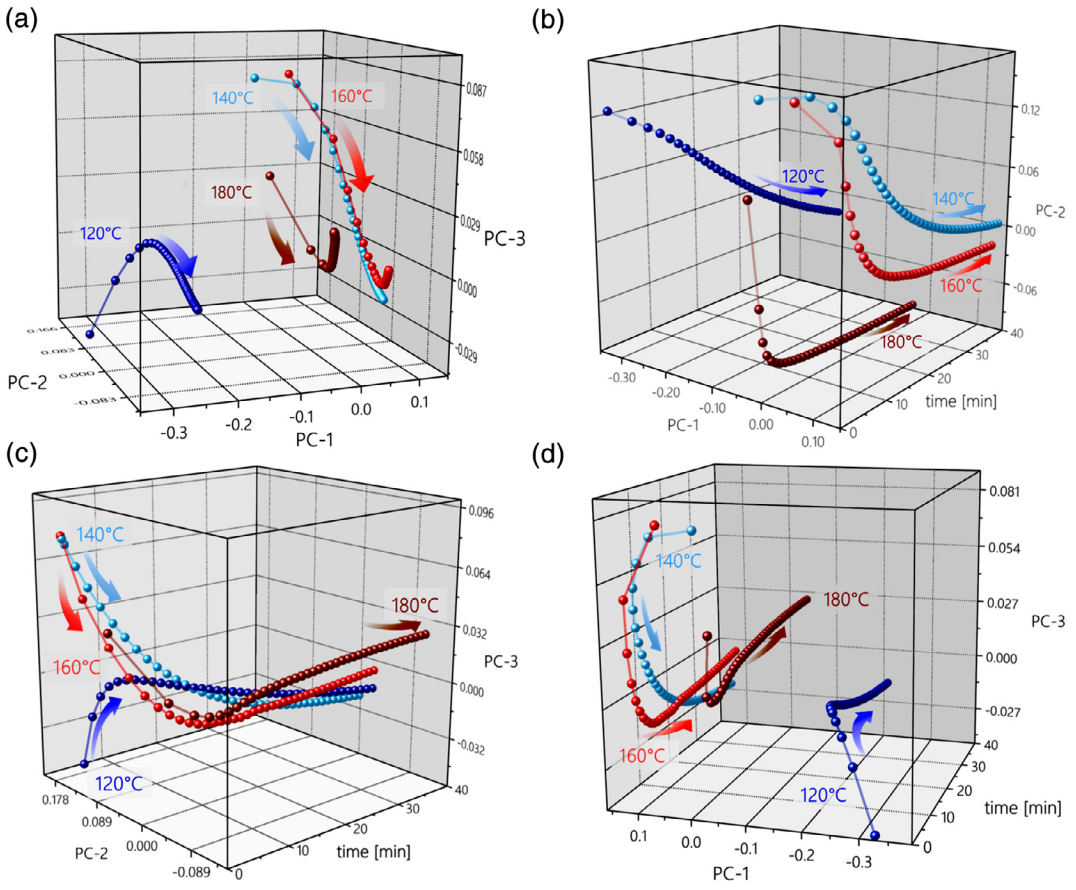


FIGURE 5 (a) Reaction course within the score space of PC1, PC2, and PC3 describing 99% of the spectra information, (b) reaction trajectories PC1, PC2 of MF resin cure in refined data space over time, (c) reaction trajectories PC2 and PC3 of MF resin cure in refined data space over time, and (d) reaction trajectories PC1 and PC3 of MF resin cure in refined data space over time. MF, melamine-formaldehyde; PC, principal component [Color figure can be viewed at wileyonlinelibrary.com]

In the plot of PC 2 and PC 3 versus time, the trajectory changes its course in the direction of the PC 3 axis. This means that the curing of MF at 180°C proceed at first very fast in the direction of decreasing scores of PC 2. This leads to the largest changes in the resin state. After that, smaller changes take place in the direction of increasing PC 3 scores. Following our earlier assignment, according to which PC-2 contains mainly information related to methylol functionalities and PC 3 predominantly represents methylene bridges, this would mean that at 180°C the initial state which is dominated by free methylol groups changes very quickly (rapid drop in methylol functionalities within the first 5 min) into a relatively stable cured state which is poor in free methylols and in which (in a second phase after 5 min), only the rearrangement of the network under formation of methylene bridges takes place.

3.3.5 | Influence of temperature on the final state of the resin

If one compares the reaction trajectories at other temperatures, significant differences in the individual processes can be seen in addition to some similar tendencies. For example, the trajectory at 120°C is completely different from that at 180°C. Particularly in the final states, these two trajectories differ considerably. In contrast to the reaction at 180°C, the reaction at 120°C does not seem to reach a stable final state after 40 min. Unlike the reaction trajectory at 180°C, the course of the reaction trajectory at 120°C in Figure 5(b) shows changes in both the PC 1 and PC 2 principle components. Furthermore, these changes do not come to an end with regard to PC 2. Figure 5(c),(d) shows that curing at 120°C leads also to a completely different final state with respect to PC 3 when compared to the trajectory at 180°C. If the course of the trajectory at 120°C were to be followed significantly longer than the 40 min reaction time, it would still not be expected that the same resin state would be achieved at the end as with the reaction trajectory at 180°C. Hence, the two curing products of the same resins will be completely different.

If one compares all individual start and end points of the trajectories shown in Figure 5, it is evident that each reaction trajectory leads to an individual end state, which differs more or less substantially from all other end points in its spectral fingerprint. Thus, each of these differently cured resins should also have a more or less different technological property profile.

The starting points are also different for each temperature, although the same starting resin was used in each case. This seems strange at the first glance. However, the different starting points of the trajectories can easily be explained. The sample is heated on the ATR cell up to the isothermal measuring temperature. During this time the sample already changes while executing the experiment. These changes will be more significant and will occur faster at higher temperatures, as we have seen in the discussion of the reaction trajectory at 180°C. Further temperature-induced changes occur while the actual spectroscopic measurement is being performed and the individual wavelength scans are recorded. All this leads to differences in the initial state of the sample at the point of the first measurement. This is reflected by the different starting points of the reaction trajectories.

From the wide variety of end points of the reaction trajectories in the data space it can be deduced, that one and the same resin may arrive at very different final network structures depending on the curing conditions. As evident from the curing trajectories in Figure 5, even if a fully cured state is obtained at a certain temperature (i.e., a stable end state where no further spectral changes can be observed), the actual chemical composition of the network formed will still be different for the same resin when cured at a different curing temperature. These differences can be described very precisely by FTIR/PCA and traced back to the processing conditions. This opens up the possibility to design the property profile of an MF resin at the stage of, for instance, laminate pressing based on reaction trajectories derived from FTIR/PCA.

If it is known (a) how a certain spectral fingerprint in the design space can be achieved (in our experimental design this is simply the combination of time and temperature) and if (b) it is further known how the spectral fingerprint correlates with a certain target property, then this target property can be specifically tailored by selecting suitable process conditions, that is, by selecting an appropriate curing trajectory that yields the desired functionality.

The reaction conditions under which a resin prepolymer is synthesized (such as the M:F ratio, pH, temperature, etc.) and also the parameter settings of further process steps (like drying, storage, etc.) will define the starting point of the curing trajectories in the design space. Hence, variations in the synthesis condition will further enhance the space of possibilities in designing resin functionality. However, as shown here, even if one and the same pre-polymer is used, many different final resin states can be produced that can spectroscopically be distinguished and correlated with process conditions as well as technological properties. Hence, the here presented methodology is especially important for end-users of resin pre-polymers that are interested in exploiting the technological potential of their multipurpose resin.

The next section shows how the spectroscopic fingerprint can be correlated with a technological property. The multivariate method PCR is used for this purpose. As a technologically relevant property, the hydrolysis stability is correlated with the spectral properties. The obtained correlation model can be used to assign technological properties to the final states of the reaction trajectories and, in turn, to select suitable curing trajectories.

3.4 | Prediction of a hydrolytic stability using PCR

Multivariate regression allows to use many even highly collinear predictor variables in the regression analysis as x-variables. Often, spectra are used as they can usually be obtained fast and highly reproducibly. The response variables on the other hand are often only obtained by complex and time consuming analytical methods.[29]

Different multivariate regression methods exist to relate the spectral information to one or several quality parameters. The quality parameter in our case will be the hydrolytic stability expressed as free formaldehyde content after acidic hydrolysis. PCR and partial least squares (PLS-R) regression are the most common multivariate methods. In comparison to common multilinear regression, highly correlated (predictor-) x-variables as common in spectroscopy can be used for PCR and PLS. In case of PCR a PCA is first performed on the original x data (spectra). The score values of the first few PCs that describe the variance of the x data well enough, are used as input x-variables in the regression analysis. One advantage is the reduction of dimensionality as only a few PCs are necessary to describe the spectra and another advantage is the orthogonality of the PCs, which reduces collinearity in the x-variables. The difficulty is to determine the correct number of PCs used for the regression to avoid under- or over-fitting. The number of PCs provides also an indicator of how robust the model and the measurement data are in Ref 29.

PLS is widely used for multivariate regression analysis, in particular for spectroscopic data. In comparison to PCR the covariance of the x and y variables are optimized in one go when calculating the PLS regression. [29] In general, care has to be taken that the spectroscopic data represent as much as possible and with high sensitivity and selectivity the target data which will be modeled by the regression analysis. In this case, the models developed by PCR and PLS often show high similarities. In case of a high discrepancy, it is advisable to improve the spectroscopic measurement setup to achieve a bias toward the target quality, for example, separating specular from diffuse reflected light or separating the elastic scattering from the inelastic absorbance of photons.[32]

In this study, we will focus on PCR to visualize and illustrate how the PCA process trajectories can be used to find a causal relationship on a molecular level between the spectroscopic data and the technological information of a target quality parameter. We will use the target quality "free formaldehyde" (as described in the materials section) determined by the acid hydrolytic degradation of the resin, which is on a molecular level synonym to other often used quality parameters like "DSC-conversion degree" or "hydrolytic stability."

The basic idea behind the wet chemical determination of the status of the cure reaction is that decorative laminates need to display a high resistance toward hydrolysis and other chemicals.[7] In order to determine macroscopically the status of the curing reaction and the surface quality of the manufactured boards, several standardized tests are used. The degree of condensation is often tested using the so-called "acid value" where a defined surface area is treated with hydrochloric acid for 15 min and afterwards, the surface is visually classified under the microscope. If the surface is strongly altered (e.g., corroded with a change in color and gloss), the resin coating was not sufficiently hardened. However, the reproducibility of this visual test is low. The determination of the curing time was optimized based on preliminary tests[24] to obtain different curing degrees as described in the experimental section. This test is more reliable than the acid test and thus will be used as the reference method and the "golden standard."

3.4.1 | Hydrolytic stability data (resp. free formaldehyde) versus DSC conversion degree

DSC experiments of thermosets are applied to describe and quantify the temperature dependence of the curing reaction and are widely accepted as a powerful tool by the scientific community as well as within the industry.[23] For MF resins, DSC measurements under isothermal conditions are difficult to analyze as generally low magnitudes of heat are generated during the curing reaction at comparatively low-reaction rates.[13] Furthermore, isothermal measurements are prone to a considerably large experimental error especially during the initial phase of the reaction due to stabilization of the oven resp. overshooting of the temperature, leading to difficulties in obtaining the exact isothermal conditions at the start of the reaction.[33] However, it is possible to perform dynamic measurements at different heating rates and to use these data to model isothermal conversion functions. The isoconversional approach (model free kinetics) to derive at model isotherms for MF cure has already been proven

successful with similar MF systems in previously published work.[13,24,33]

In Figure 6, the free formaldehyde content is plotted versus the corresponding conversion degree (respective time and temperature treatment) obtained from DSC model-free kinetic analysis (MFK) data without further data pre-treatment. As can be seen in the figure, the higher the applied curing temperature, the higher is the hydrolytic stability leading to a lower amount of formaldehyde (FA) liberated during acidic treatment. For samples treated with 100 and 120°C, around 7 wt% of FA were liberated from the solid resin samples. In contrast, the samples treated with 140–180°C exhibited much higher resistance against acidic hydrolysis. The conversion degree based on iso-conversional kinetics calculated from DSC experiments increases as well with increasing curing temperature. At 160 and 180°C, a curing degree (resp. conversion degree) above 90% is predicted as shown in Figure 6.

For samples cured between 120 and 160°C, an almost linear relationship between the conversion degree and the free formaldehyde content is visible. However, at low-curing degrees (e.g., below 120°C) and at very high-curing degrees above 90% (e.g., above 160°C), there are significant deviations from this linear relationship. The linear model completely fails to describe hydrolytic stability at higher temperature (180°C). Thus, curing reactions above 160°C and below 120°C may show a different mechanistic structure than at the mean standard temperatures around 140°C.

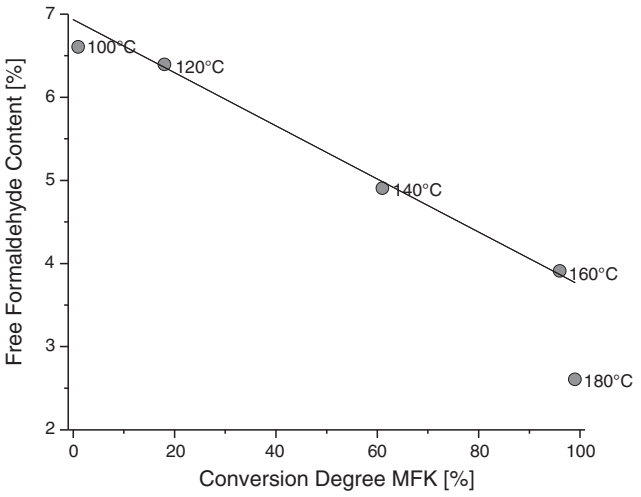


FIGURE 6 Content of free formaldehyde after acidic hydrolysis of resin samples cured at different temperatures over conversion degree determined by DSC/MFK data. The trend line is only calculated up to the temperature of 160°C. The predictions made by DSC/MFK fail to describe the hydrolytic behavior at higher temperatures. DSC, differential scanning calorimetry; MF, melamine-formaldehyde

These results lead to the assumption that the resistance to hydrolysis depends not only on the overall curing degree but also on the formed chemical network, which may consist of different fractions of methylol-entities, ether- or methylene bridges and different types of the cross linkages formed within the network structure. This is also in accordance with the literature.[10] Thus, the sum parameter "conversion degree" obtained from DSC measurements is not suitable to describe in full detail the chemical network structure. Spectroscopy on the other hand provides information on the complex chemical and morphological structure and thus should be able to predict more reliably the hydrolytic stability of the samples together with a sound and causal interpretation of the network structure on a molecular level.

3.4.2 | Correlation of spectral data with the hydrolytic stability quality parameter using spectroscopic process trajectories: PCR

The free formaldehyde content of the hydrolysis tests is used as response variable y. As predictor variables X, the FTIR spectra during resin cure is used at the respective time and temperature treatment as described in the materials section. The entire fingerprint area from 1670 to 700 cm^{-1} is used for the calculation. In Figure 7(a), the predicted free formaldehyde measurement of the model with three PCs is displayed versus the measured value of the free formaldehyde as the calibration standard. The importance of certain wavelength regions to predict the free formaldehyde after acid hydrolysis is presented by the PCR regression coefficients (Figure 7(b)). The results of the calculations are summarized in Table 1.

The residual validation variance is at a minimum when using three PCs. If more PCs are included in the model, no further improvements can be achieved. The root means square error of calibration for 3 PCs is 0.13%, which is comparable to the reproducibility of the reference method. The root means square error of cross validation (RMSECV), is 0.35%, which is still less than 7% of the mean hydrolytic stability. R-squared for calibration is 0.99 and for cross validation 0.96. It is important to emphasize, that this error is dominated by the error of the wet chemical analysis and not by the spectroscopic measurement, which show a high reproducibility.

For positive absorbance spectra, absorption in the area of positive coefficient numbers increase the y values, if the response is also positive. Whereas, higher absorption in the area of negative coefficients decrease the value of the response variable. The regression plot (Figure 7(b)) is dominated by two peaks at around 1000 cm^{-1} (methylol entity) with positive values and the X-sensitive

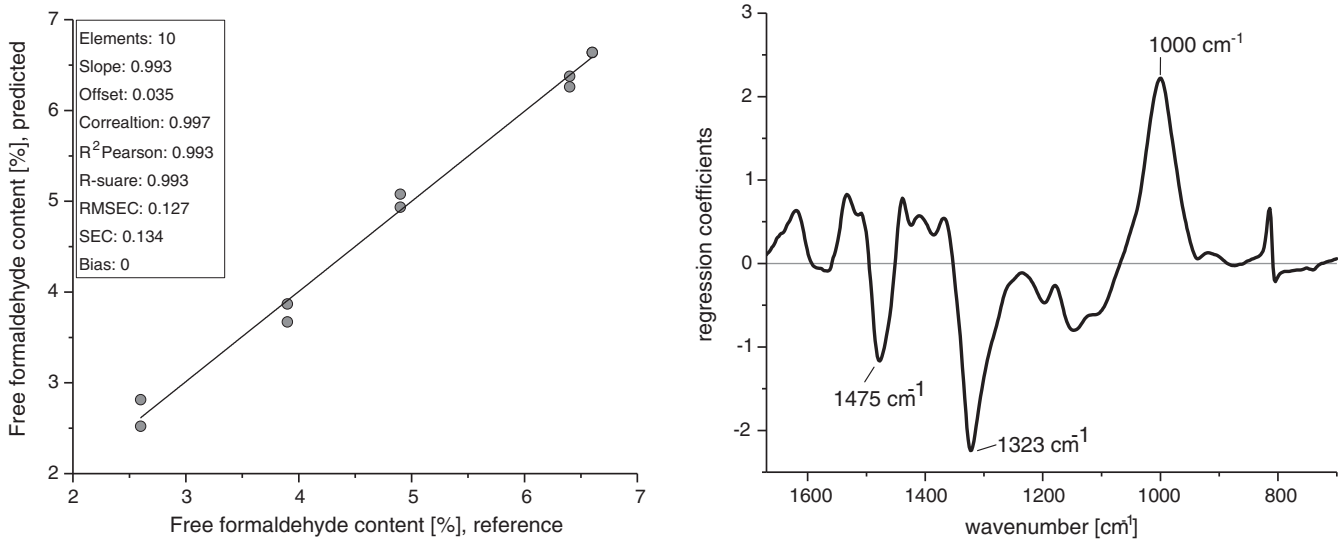


FIGURE 7 PCR results calculated with three PCs; (a) predicted versus reference values of hydrolytic stability and (b) regression coefficients for the IR spectra. PC, principal component; PCR, principal component regression

TABLE 1 Results of the PCR analysis to predict the free formaldehyde liberation after acidic hydrolysis

Factors	Contribution of individual single factor x variance %	Cumulative x variance %	Contribution of individual single factor y variance %	Cumulative y variance %	R^2 (calib)	R^2 (valid)	RMSE (calib) %	RMSE (valid) %
1	83	83	58	58	0.58	0.54	0.99	1.18
2	12	95	37	95	0.95	0.92	0.33	0.48
3	4	99	4	99	0.99	0.96	0.13	0.35

Abbreviation: RMSE, root mean square error.

C_{Ar}-N absorption band in the region of 1350–1315 cm^{-1} with negative values. The latter peak is affected by the nature of the substituent at the amine function and a shift indicates the formation of bridged species during condensation.

This means that a high-residual methylol-component results in a high liberation of free formaldehyde by acidic hydrolysis. Interestingly, the area of symmetric ether band vibrations at around 1040 cm^{-1} is included in this band. It is well known, that with increasing curing temperature and time, the liberation of the free formaldehyde is lower and thus the peak at around 1325 cm^{-1} is negatively correlated for the ether resp. methylen-groups.

There are indications that the wavenumber range between 1400 and 1600 cm^{-1} may also be a good indicator for the transition from the ether bridges to more methylene-bridges at higher curing temperatures, which would also fit into the mechanistic picture of the curing reaction. This shows, that the type and quantity of bridges formed during network formation influence the stability toward hydrolysis as well, which is also in accordance with the literature[10] and as shown in the PCA-section of this article is explained and measured on a molecular level.

Table 1 shows the results of the PCR analysis and their cumulative x- and y-variance for this data set. With three PCs an adequate model can already be formed and a very high percentage of x and y variance can be explained. Hence, the risk of overfitting is limited and the calibration error is also low. Table 1 shows the explanation of the variance in the data set in percentage for different chemometric models, each differing in the number of PCs used for the model. The column "contribution x variance %" and "cumulative x variance %" show respectively the explanation fraction of a single PC on its own and of the model containing the corresponding number of PCs (cumulative). The cumulative explained variance indicates that a model with only one PC (factor) explains the data set (or the variance in the data set) to 83%, a model with two factors then explains it to 83

+ 12%, that is, it has a significantly higher explanatory value overall. The model with three factors, which was used here to describe the data set, has an explanatory value of 99%. This means that the model is able to summarize and describe practically the entire variance in the data set with only three independent descriptors.

Furthermore, it can clearly be seen, that the proportion (%) between PC1 and PC2 changes between the measured spectral x-variance information of the PCA analysis and the y-variance to predict the hydrolysis resistance. Ether and methylene bridges formed within the used temperature range seem to be more important to explain the hydrolytic resistance of the coating. The hydrolytic stability can even be quantified with the spectral analysis. Thus, most importantly, a robust model can be established that can be used to control and predict the quality of the thermoset even on an industrial level.

4 | CONCLUSION

The curing reaction of MF resins results in a highly complex network structure with different contributions of several chemical moieties as, for example, methylol, ether, and methylene bridges. In this context, IR spectroscopy provides many advantages and yields detailed complex chemical information, which is difficult to interpret on a univariate basis using single entities. The study shows that a univariate peak analysis to monitor and analyze the reaction is not conducive due to strong overlaps of the spectral regions of interest. Therefore, a MVA approach is used to describe the reaction trajectories during MF resin cure at different temperatures. PCA allows to display the reaction trajectories during the network formation in the reduced data space of the calculated PCs. In this way, the progression of the curing reaction can be monitored and the chemical composition at each point of the trajectory can be characterized. Different curing conditions can be compared directly within this data space.

The FTIR spectra also provide a promising data basis in the future, which allows prediction to be made concerning macroscopic resin properties (quality parameters) on the basis of molecular patterns. This is shown by multivariate regression methods. The spectral patterns are quantitatively correlated to the hydrolytic stability of differently cured MF resins. This could be the basis for future studies to design resin properties depending on the incoming material (defined conversion degree of starting material) via application of appropriate processing parameters. The application of PAT concepts and toolboxes will be essential for the production of the future to gain competitive advantages.

The procedure shown in this paper for the quantification of the influence of chemical and morphological features of the coating on a molecular level provides a deep insight into the mechanistic and thus causal relationship of complex quality criteria. Furthermore, using the multivariate regression analysis a multitarget optimization may also be possible to design coatings with a defined multiple target profile for a future individualization of product properties and mass customization.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the COMET program Wood, project number 865 905, of the Austrian Research Promotion Agency (Österreichische Forschungsförderungsgesellschaft) FFG Grant: COMET Wood 865 905 managed by Wood K plus–Competence Center for Wood Composites & Wood Chemistry, Linz, Austria, Area Wood & Paper Surface Technologies. The authors would like to thank all their industrial partners, who co-financed this project. WOA Institution: HOCHSCHULE REUTLINGEN. Blended DEAL: Projekt DEAL.

ORCID

Andreas Kandelbauer https://orcid.org/0000-0001-9786-964X

REFERENCES

[1] A. Kandelbauer, A. Teischinger, *Eur. J. Wood Wood Prod.* **2010**, *68*, 179.
[2] R. W. Kessler, *J. Chemom.* **2013**, *27*, 369.
[3] R. W. Kessler, W. Kessler, E. Zikulnig-Rusch, *Chem. Ing. Tech.* **2016**, *88*, 710.
[4] J. Claßen, F. Aupert, K. F. Reardon, D. Solle, T. Scheper, *Anal. Bioanal. Chem.* **2017**, *409*, 651.
[5] A. Pizzi, K. L. Mittal, *Handbook of Adhesive Technology*, 2nd ed., Marcel Dekker, New York **2003**.
[6] R. J. Roberts, P. D. Evans, *Compos. Part A Appl. Sci. Manuf.* **2005**, *36*, 95.
[7] A. Kandelbauer, G. Wuzella, A. Mahendran, I. Taudes, P. Widsten, *J. Appl. Polym. Sci.* **2009**, *113*, 2649.
[8] R. Braun, A. Denk, N. Kalwa, EP 3238934 **2017**.
[9] M. L. Scheepers, J. M. Gelan, R. A. Carleer, P. J. Adriaensens, D. J. Vanderzande, B. J. Kip, P. M. Brandts, *Vib. Spectrosc.* **1993**, *6*, 55.
[10] G. Coullerez, D. Léonard, S. Lundmark, H. Mathieu, *J. Surf. Interface Anal.* **2000**, *29*, 431.
[11] J. R. Ebdon, B. J. Hunt, W. T. S. O'Rourke, J. Parkin, *Br. Polym. J.* **1988**, *20*, 327.
[12] A. Bogomolov, *Chemom. Intell. Lab. Syst.* **2011**, *108*, 49.
[13] W. Kohl, J. Frei, B. Trethewey, *Tappi J.* **1996**, *79*, 199.
[14] G. Wuzella, A. Kandelbauer, A. R. Mahendran, A. Teischinger, *Prog. Org. Coatings* **2011**, *70*, 186.
[15] A. R. Mahendran, G. Wuzella, A. N. A. Kandelbauer, *J. Therm. Anal. Calorim.* **2012**, *107*, 989.
[16] R. Hardis, J. L. P. Jessop, F. E. Peters, M. R. Kessler, *Compos. Part A* **2013**, *49*, 100.
[17] C. Hirschl, M. Biebl-Rydlo, M. DeBiasio, W. Mühleisen, L. Neumaier, W. Scherf, G. Oreski, G. Eder, B. Chernev, W. Schwab, M. Kraft, *Sol. Energy Mater. Sol. Cells* **2013**, *116*, 203.

[18] A. Kandelbauer, G. Wuzella, E. Dolezel-Horwath, R. W. Kessler, *Chem. Ing. Tech.* **2010**, *82*, 537.
[19] E. Frauendorfer, W.-D. Hergeth, *Anal. Bioanal. Chem.* **2017**, *409*, 631.
[20] G. E. Myers, J. A. Koutsky, *For. Prod. J.* **1987**, *37*, 56.
[21] EN 717–3 Formaldehyde release by the flask method **1996**.
[22] S. V. Vyazovkin, A. I. Lesnikovich, *Thermochim. Acta* **1992**, *203*, 177.
[23] S. Vyazovkin, *Isoconversional Kinetics of Thermally Stimulated Processes*, Springer International, Heidelberg, New York **2015**.
[24] S. Weiss, K. Urdl, H. A. Mayer, E. M. Zikulnig-Rusch, A. Kandelbauer, *J. Appl. Polym. Sci.* **2019**, *136*, 47691.
[25] Socrates, G. *Infrared and Raman characteristic group frequencies*; Wiley, Chichester New York **2004**.
[26] L. Kutuzova, K. Athanasopulu, M. Schneider, A. Kandelbauer, R. Kemkemer, G. Lorenz, *Curr. Dir. Biomed. Eng.* **2018**, *4*, 535.
[27] M. Sahin, S. Ayalur-Karunakaran, J. Manhart, M. Wolfahrt, W. Kern, S. Schlögl, *Adv. Eng. Mater.* **2017**, *19*, 1600620.
[28] J. Santos, J. Pereira, N. Paiva, J. Ferra, F. D. Magalhães, J. M. Martins, L. H. P. de Carvalho, *Inst. Mech. Eng. Part C J. Mech. Eng. Sci.* **2020**, *0*, 1.
[29] W. Kessler, *Multivariate Datenanalyse für die Pharma-, Bio- und Prozessanalytik*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim **2007**.
[30] R. Bro, A. K. Smilde, *Anal. Methods* **2014**, *6*, 2812.
[31] I. H. Anderson, M. Cawley, W. Steedman, *Br. Polym. J.* **1969**, *1*, 24.
[32] R. W. Kessler, W. Kessler, in *Comprehensive Chemometrics: Chemical and Biochemical Data Analysis*, 2nd ed. (Eds: S. Brown, R. Tauler, B. Walczak), Elsevier, Amsterdam **2020**, p. 237.
[33] A. Kandelbauer, G. Wuzella, A. Mahendran, I. Taudes, P. Widsten, *Chem. Eng. J.* **2009**, *152*, 556.

How to cite this article: Weiss S, Seidl R, Kessler W, Kessler RW, Zikulnig-Rusch EM, Kandelbauer A. Multivariate process trajectories for molecular description of MF thermal curing and correlation with hydrolytic stability. *J Appl Polym Sci*. 2021;e50635. https://doi.org/10.1002/app.50635