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Multivariate Curve Resolution (MCR) of real-time infrared spectra for analyzing the curing behavior of solid MF thermosetting resin

Stephanie Weiss [a,d], Regina Seidl [a,d], Waltraud Kessler [b], Rudolf W. Kessler [b], Edith M. Zikulnig-Rusch [a], Andreas Kandelbauer [c,d,*]

[a] *Kompetenzzentrum Holz GmbH, Altenberger Straße 69, 4040 Linz, Austria c/o Area 3, Klagenfurter Straße 87 – 89, 9300, St. Veit an der Glan, Austria*
[b] *Kessler ProData GmbH, Kaiserstraße 66, 72764, Reutlingen, Germany*
[c] *Lehr und Forschungszentrum Process Analysis and Technology (LFZ PA&T), School of Applied Chemistry, Reutlingen University, Alteburgstraße 150, D-72762 Reutlingen, Germany*
[d] *Institute of Wood Technology and Renewable Materials, Department of Material Science and Process Engineering, BOKU-University of Natural Resources and Life Sciences, Konrad Lorenz Strasse 24, A-3430 Tulln, Austria*

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ABSTRACT

The isothermal curing of melamine resin is investigated by in-line infrared spectroscopy at different temperatures. The infrared spectra are decomposed into time courses of characteristic spectral patterns using Multivariate Curve Resolution (MCR). It was found that depending on the applied curing temperature, melamine films with different spectral fingerprints and correspondingly different chemical network structures are formed. The network structures of fully cured resin films are specific for the applied curing temperatures used and cannot simply be compensated by changes in the curing time. For industrial curing processes, this means that cure temperature is the main system determining factor at constant M:F ratio. However, different MF resin networks can be specifically obtained from one and the same melamine resin by suitable selection of the curing time and temperatures profiles to design resin functionality. The spectral fingerprints after short curing time as well as after long curing time reflect the fundamental differences in the thermoset networks that can be obtained with industrial short-cycle and multi-daylight presses.

1. Introduction

Melamine formaldehyde (MF) resins are in industrial use for nearly 90 years. They appear in many interior and exterior applications because of their exceptional properties. In particular, MF resins are used as adhesives in the wood based panel industry for gluing particle boards and, most importantly, as surface coatings for the production of decorative laminates in which wood based panels are coated with MF impregnated decorative paper sheets [1].

Production of such impregnated paper is usually carried out in two steps [1–4]. First, the paper core is impregnated and filled with urea-formaldehyde (UF) or MF resin and pre-dried at elevated temperatures from 70 to 190 °C in an oven [3,5,6]. In a subsequent second step, the paper is coated with another layer of MF resin and again dried to a desired moisture content [3,7,8]. These impregnated sheets are further used as solid, self-gluing coating films for suitable carrier materials in a hot press [3,4,7]. The conditions in the hot press for laminate production vary depending on the requirements of the final product. For short-cycle pressing conditions, usually temperatures in the range from 170 to 190 °C are applied for 30–60 s. Multi-stage presses use much longer time cycles ranging from 30 to 90 min at lower temperatures of about 150 °C and enable, for instance, the production of high-gloss surfaces by suppressing evaporation of steam by cooling the laminates still under pressure [9].

The MF pre-polymer in the impregnated paper consists of a complex mixture of oligomeric compounds and network fragments. Thermal cross-linking leads to rather complex chemical network structures that are greatly influenced by the applied curing conditions and are difficult to predict. The specific chemical structure and the extent of curing of the coated resin have a great influence on the surface properties of the final product such as thermal stability, resistance to hydrolysis or stability during further processing of the laminates (e.g. sawing, drilling) [8,10,

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[*] Corresponding author. Lehr und Forschungszentrum Process Analysis and Technology (LFZ PA&T), School of Applied Chemistry, Reutlingen University, Alteburgstraße 150, D-72762 Reutlingen, Germany

E-mail address: andreas.kandelbauer@reutlingen-university.de (A. Kandelbauer).

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11]. They need to be carefully adjusted depending on the desired final performance profile.

Although the surfaces of a wide range of different products show very specific performance characteristics, they may all be produced from one and the same base melamine formaldehyde pre-polymer mainly by engineering the curing conditions and, in turn, the crosslinking state of the employed MF resin. Each of the MF-based products listed in Table 1 has a very well defined, highly specialised property profile tailored to the particular application. For example, MF surfaces for laminate floorings must have exceptionally high abrasion resistance, while high scratch resistance is more important for vertical furniture fronts. On the one hand, whiteboards must be very easy to write on and it must be possible to remove the writing again and again without leaving any residue, whereas writeability is completely unimportant for drilling entry boards employed in the electronic industry to assist drilling of stacks of printed circuit boards. High weather resistance is very important for surfaces of exterior cladding elements in outdoor areas, whereas especially high chemical resistance is more important for work surfaces for laboratory furniture. In principle, all these properties can be achieved with the same melamine resin if it is possible to optimally adjust the curing state and the chemical characteristics of the formed network structure accordingly.

However, the selection of specific curing conditions for individual product types today is still mostly based solely on many years of experience in industrial practice and does not yet follow a reliable, knowledge-based development process. This is due to the fact that it is analytically very demanding to monitor the final process step (the thermal curing in a hot press) accordingly or to reproduce it in the laboratory. While comparatively much is known about the chemical processes that take place during the synthesis of the prepolymer in the liquid and largely low-molecular or oligomeric state of the melamine-formaldehyde systems, there is relatively little information about the actual curing process itself and the chemical changes taking place in this phase. This is very unfortunate in that, although the basic property profile of a MF resin is largely predetermined via the synthesis conditions (via choice of the M:F ratio and the reaction conditions), this general property profile is still too imprecise for the customer-oriented, tailor-made fine-tuning of the product properties and leaves too high a margin for the narrow quality criteria and customer requirements. The final application properties of a MF surface are still significantly influenced and ultimately determined during the final hot curing step. This is the more important since only a limited number of different MF resin types are usually used for the large variety of products, or only one base melamine resin at all, so that achieving tailored product properties is mainly or exclusively based on the choice of appropriate curing conditions and being able to engineer the curing conditions is crucial [12–15].

Therefore, it is desirable to have a science-based approach for the specific adjustment of the functionality of a surface and to be able to derive the expected product properties from objective measurement data. For manufacturers, it would be highly beneficial to determine the performance of a final product in advance and to be able to adjust the curing conditions in response to both, variations in the incoming material and the targeted final resin property profiles, thereby allowing a more flexible production flow [15–17]. The present work aims to contribute to the knowledge-based functionality design of MF surfaces.

Table 1
Different product types carrying MF surfaces with different tailored property profiles.

Product Type	Main performance characteristics
Vertical furniture surface	High transparency, good scratch resistance
Laminate flooring	Wear resistance, high abrasion resistance, high transparency
White boards	Good writability and cleanability for many write/erase-cycles
Table tops for kitchen furniture	Good temperature stability, hot steam resistance, hydrolytic stability
Working Surfaces for Laboratory furniture	Very high chemical resistance, good temperature stability, solvent and acid/base stability
Surfaces for exterior cladding	High durability, light fastness, hydrolytic stability
Surfaces for bathroom interior	hydrolytic stability
Drilling entry boards for the electronic industry	Mechanical stability, favorable tear out behavior, no resin smear upon drilling, optimized brittle fracture behavior

In previous studies on the curing of MF networks it was found that mid-infrared spectroscopy allows the study of the chemical structure of cured MF resins in great detail [18,19]. ATR technology was chosen to mimic the industrial conditions during the pressing process in the hot press. It was shown that the main structural features in cured MF networks are free methylol groups, methylene bridges and methylene ether bridges. Their relative abundance governs the performance characteristics of the surface film. The aim of the present study is to illustrate how the chemical features of cured MF films obtained with one and the same MF pre-polymer can be tuned by the thermal curing conditions on the basis of spectral fingerprints and curing trajectories as measured by Fourier Transform infrared spectroscopy.

2. Materials and methods

2.1. Chemicals

Kauramin® 773 was obtained as a powder from BASF (M:F = 1.6). The powder was used directly for the measurements.

2.2. Infrared spectroscopy and sample preparation

ATR FTIR spectroscopy measurements were performed on a Bruker Tensor 27 (Bruker Optik GmbH, Ettlingen, Germany) with a “Golden Gate Heated Diamond Top Plate” using the OPUS 2.7 software package. Isothermal treatment was performed at different temperatures (120, 130, 140, 150, 160, 170, 180 °C). The MF pre-polymer powder was placed on top of the plate at the respective temperature without any pretreatment. Curing of solid MF under isothermal conditions is performed on an ATR measuring cell where a solid resin sample is pressed onto the ATR crystal during cure at temperatures covering the relevant temperature ranges applied in industrial curing protocols with short-cycle and long-term pressing programs. Pure MF resin films are cured as model systems to focus on the principal chemical changes in MF resins during cure. The fast short-cycle programs are mimicked by the initial phase of the curing profiles. Here, the higher temperatures are of particular interest. For long-term press cycles which can last by far more than 30 min, the final reaction phase of the curing profiles (resin state after 45 min) is mainly discussed. The average temperature for multistage pressings is around 150 °C, hence, here the temperature range of 150 ± 30 °C is focused to gain better insight into the chemical changes taking place.

Spectra were recorded every minute in the range from 4000 to 600 cm^{-1} against air as the background spectrum with a resolution of 4 cm^{-1} and a scan rate of 32 scans per spectrum. All measurements were performed at least two times and the mean value of the resulting spectra was used for further processing.

2.3. Data analysis – multivariate curve resolution

Multivariate data analysis of the IR spectra was performed using the Unscrambler® X 10.4 software package (Camo Analytics, Oslo, Norway). The fingerprint region of the obtained spectra from about 1670 to 700 cm^{-1} was analyzed. Normalized (unit vector normalization) spectra were used for further chemometric analysis. During this study, non-negativity of spectra and concentrations and closure were applied as constraints, no a priori assumptions (e.g. pure component spectra) were made.

3. Results and discussion

3.1. *MF spectra at a selected temperature of 150 °C during the isothermal curing reaction with band assignment*

The used resin was cured under isothermal conditions at different temperatures. Real-time FTIR spectra were recorded during network formation. The normalized spectra measured at 150 °C are displayed in Fig. 1 as representative examples. For chemometric analysis, the fingerprint region of the IR spectrum from about 1670 to 700 cm^{-1} was exploited, as it provides in-depth information on the changes of chemical composition during cross-linking [18].

The triazine ring shows two typical bands at 1540 cm^{-1} and at 810 cm^{-1} due to stretching vibrations and out-of plane bending vibrations of the ring. These signals do not undergo any changes during cross-linking. Other bands, however, show very characteristic changes: The C–O stretching vibration of the methylol function at about 990 cm^{-1} decreases with progressing curing time, as the methylol moieties react to form methylene and methylene-ether bonds. A decrease in relative concentrations of primary amines is indicated by the disappearance of the small shoulder at 1630 cm^{-1}. The formation of bridged species is clearly visible by the position the C_{Ar}-N absorption at about 1360 cm^{-1}. This X-sensitive band shifts to lower wavenumbers (1320 cm^{-1}) due to the change of the substituent at the amine function. Other C–N vibrations occur at about 1150 cm^{-1}. Within the region of about 1150 to 1030 cm^{-1}, C–O–C stretching vibrations of ether moieties are present in the spectrum. The formation of methylene-ether bonds leads to increasing band intensities within this region. In particular, the increase of the symmetric vibration band at about 1040 cm^{-1} can clearly be seen in the spectra. Within the region of the strong bands from about 1550 to 1400 cm^{-1}, several C–H vibrations are present due to the $-CH_2$ moieties of methylol, methylene-ether and methylene moieties. However, a clear distinction of the different species is difficult [18,20].

Qualitatively similar absorbance bands and band shifts are observed with the time courses performed at the other temperatures.

3.2. *Multivariate curve resolution (MCR) as a tool to extract molecular information from complex data*

3.2.1. *General procedure*

During the curing of MF resins, the formation and evolution of a chemical network is monitored. At the beginning of the actual curing in a heated tool (the thermosetting process), the resin is present as an oligomeric, partly cross-linked pre-polymer consisting of several covalently linked melamine cores. During the condensation reaction, no pure, isolatable chemical species or simple molecular intermediates are formed, but rather a mixture of all chemical species making up the resin is present at all times. Hence, a mixture of methylol-moieties, methylene bridges, methylene-ether bridges, different amine functions and various C–H bonds can be expected at any instant of curing. Throughout the reaction course, only the relative proportions of these chemical functionalities change.

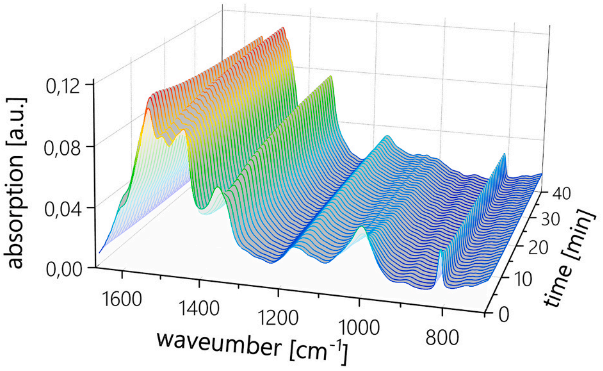

Fig. 1. Cure monitoring of MF resin under isothermal conditions at 150 °C for 40 min using real-time FTIR spectroscopy.

The resulting IR spectra represent the sum of all species present at a specific point during the reaction course. Hence, changes in the spectra represent a change of the relative ratios of the involved chemical species. The spectroscopic signatures of the individual chemical functions are very similar to each other. This results in complex, superimposed spectra. Hence, it is difficult to assign the various bands to a specific network type with a univariate data analysis approach. Using MCR, generally enables the extraction of individual compounds from a complex spectral matrix and to quantitatively display the changes in chemical composition during a reaction [21–23]. However, it is not possible to extract individual chemical compounds from such a complex mixture like in the present case of gelled resin networks since there are no physically separable entities anymore. Rather, spectral patterns that concertedly change during the reaction course are extracted in the present case. These patterns are like fingerprints that characterize a certain network type and contain the spectral information on the relative abundance of the chemical functionalities.

The absolute share of any individual chemical species (e.g., the number of methylol groups) is of minor importance but the change of the network composition itself is of great interest. To which extent the groups change depends on several factors like reaction conditions, melamine to formaldehyde ratio or used additives. Hence, during different reaction steps, some chemical groups are more strongly represented than other groups.

We have seen elsewhere [24] that under different curing conditions spectral components resembling network types with predominantly methylol (OL-type), methylene-ether bridges (ET-type) and methylene functions (MN-type) can be extracted from the reaction spectra. The specific ratio between the three components, i.e. the finally achieved curing state, depends on the applied curing conditions.

The true value of the concentrations might not match the value estimated from the spectroscopic share exactly. The higher the polarity of a chemical bond, the higher is the intensity of the spectroscopic signature in the IR spectrum. For example, methylol compounds possess a higher absorbance coefficient ε and will be over-represented in the spectrum compared to other chemical moieties. However, it is expected that the concentration profiles of the network types calculated from the spectra will not differ much from the real-life concentrations.

In MCR it is important to select an appropriate number of orthogonal components so that the model is neither under- nor overfitted. In our case, three components are used to describe the data set, as the lowest value of total residual (1×10^{-5}) was achieved with 3 components. Including a fourth component results in an increase of the total residuals which indicates overfitting. This also makes sense from a chemical point of view, because only three main functionalities, namely methylol-moieties, methylene bonds and methylene-ether bridges, are expected. Furthermore, a detailed spectral analysis of the fourth component spectrum has shown that this component only represents a correction on the other component spectra and does not carry the characteristics of a new chemical entity.

3.2.2. *Component spectra - feature extraction and comparison to IR spectra*

In the first step, the band assignment of the calculated component spectra (Fig. 2) was done. The spectra represent the typical spectral patterns of the individual components and can be interpreted similar to IR spectra.

The calculated spectrum of the first component (see blue line in Fig. 2) is dominated by the strong C–O vibration band at 990 cm^{-1}. The C_{Ar}-N band is present at 1360 cm^{-1} and the band at 1620 cm^{-1} that can be attributed to primary amines is clearly visible. The CH_2 vibration is present at 1440 cm^{-1}. The component spectrum resembles the starting material very well. This component will further be referred to as OL

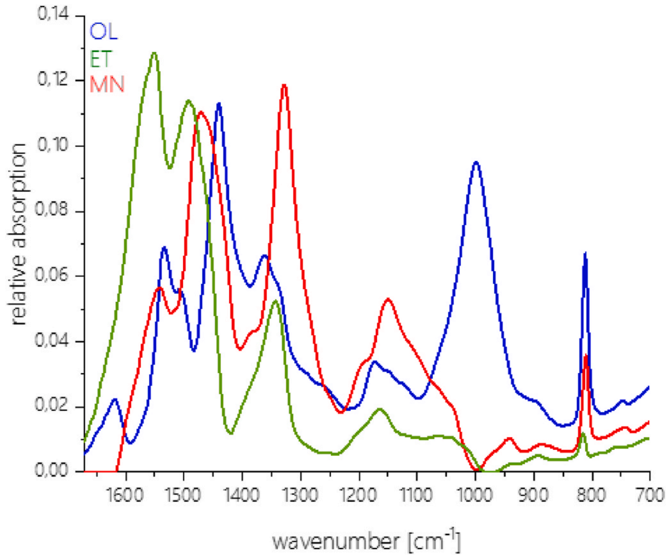

Fig. 2. Calculated component spectra using MCR with three components of real-time FTIR spectra during resin cure.

component due to the high amount of methylol moieties in the resin network.

The second component (see green line in Fig. 2) does not show strong methylol vibrations. However, significant absorptions in the area of ether bonds in the spectral region from 1100 to 1000 cm^{-1} (C–O–C vibrations) are present. The C_{Ar}-N vibration is shifted to about 1345 cm^{-1} and the CH_2 moiety is present at 1490 cm^{-1}. This component can be assigned to a network with a higher proportion of methylene-ether bridges and is abbreviated in the following as the ET network.

The third component (see red line in Fig. 2) shows no C–O vibrations of primary alcohols. The C_{Ar}-N vibration band has changed its position considerably to 1330 cm^{-1}. Further strong bands in the region of 1200 to 1000 cm^{-1} are present. The C–H vibration of the CH_2-moiety is present at 1470 cm^{-1}. This spectrum can be attributed to a network with a higher amount of methylene bonds due to the strong shift of the C_{Ar}-N band compared to the starting material. It will be referred to as the MN network in the following subsections.

3.2.3. Component concentrations vs. time - kinetic analysis of the reaction course for selected temperatures

To gain an impression of the reaction courses at different temperatures, the results of the reactions at 130, 150 and 170 °C are discussed, since they reflect the general trends well. In Fig. 3, the temporal courses of the three orthogonal components OL, MN and ET are shown.

The general profiles of the concentration courses are very similar for all temperatures. The absolute concentrations of the different network types, however, differ considerably, in particular at the initial and final phase of the reaction.

The component concentrations show strong changes within the first minutes at the beginning of the reaction. However, during the

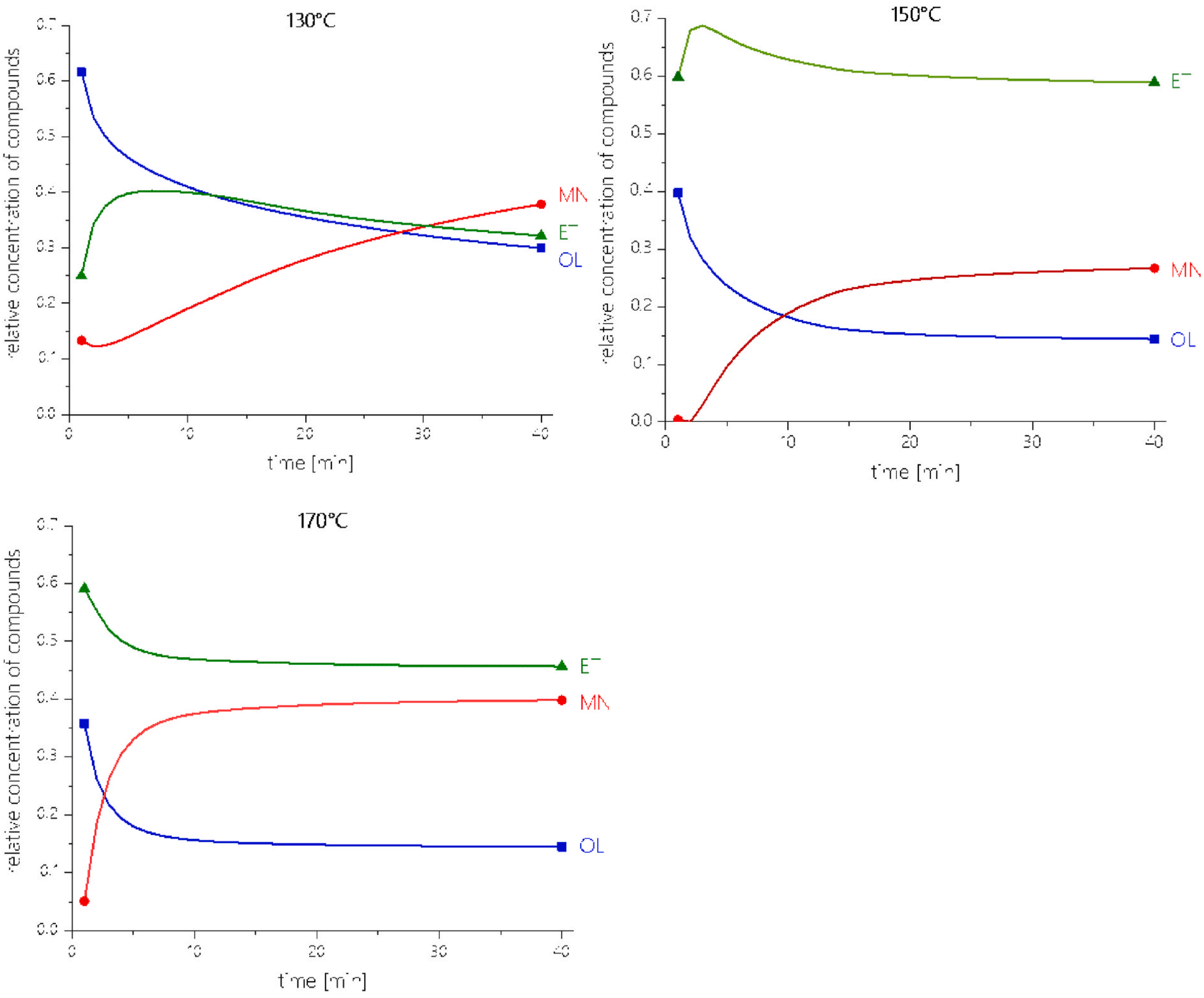

Fig. 3. Component concentrations of the three components OL, MN and ET of MCR calculation over time for the selected temperatures 130, 150 and 170 °C.

concentration course profile, nearly constant values of the component concentrations are reached. While the concentration course of the OL and MN networks decrease or increase, one can clearly see that the ET component is a result of a consecutive reaction. The time to reach a near-equilibrium state depends strongly on the applied temperature. The higher the temperature, the faster a constant concentration is reached. However, at lower temperatures (<140 °C), this near-constant state is not yet reached within the observed time period of 40 min.

The start (1 min) and the end point (40 min) of the profiles are marked and will be further discussed in the following paragraphs.

3.2.4. Comparison of component concentration at the beginning and at the end of the reaction

The component concentrations in % at the beginning of the reaction after 1 min and at the end point of the reaction after 40 min are compared for each temperature (see Fig. 4). Both graphs show that basically all three components are always present over the entire temperature range. However, the relative ratios change from the start point to the end of the reaction together with increasing temperature.

The composition at the starting point (first spectrum) depends strongly on the curing temperature. The ATR accessory is preheated to the respective temperature before the sample is placed on the device. The first spectrum is recorded with a time lag of 1 min from sample application where already curing takes place. Depending on the applied temperature, the samples experience a different energy input during heating. The higher the temperature difference, the faster temperature-dependent processes like curing or evaporation of volatile components take place. At the end of data acquisition after 40 min reaction time (last spectrum), the species distribution varies greatly depending on the applied temperatures.

The concentration of the OL network with a high amount of methylol moieties is high at the beginning of the reaction and decreases for all experiments until the end of the reaction due to the formation of methylene-ether and methylene bridges. This is shown in Fig. 4 by comparing the characteristics of the blue curve left (1 min) with the blue curve right (40 min). Generally, the amount of OL is higher for samples cured at lower temperatures. However, even at high temperatures of 180 °C, the OL component is still present with a share of 15–20% at the end of the reaction.

The ET component with a higher amount of methylene-ether bridges stays nearly constant when the concentration at the reaction start is compared to the final value (green curve left vs right in Fig. 4). At higher temperatures above 150 °C, the concentration slightly decreases compared to the initial value. Methylene-ether bridges are mainly formed at intermediate temperatures (140–160 °C) and in particular already at the start of the reaction.

The amount of the MN network increases as curing progresses with time. Surprisingly, at 120 and 130 °C already a significant amount of methylene bridges is present at the end of the curing reaction. The relative amounts of MN are lowest at the temperatures between 140 and 160 °C. At increasingly higher temperatures the spectrosscopic concentration of the MN-rich network type becomes higher und is the most prevalent type of network at the end of cure (in the resin cured at 180 °C for 40 min).

It was shown earlier that good hydrolytic and chemical stability is associated with high levels of the MN-network component [25] and that hydrolytic stability against acid attack can be quantitatively predicted and modeled based on the spectral patterns of the cured MF films. This means that resin films cured under conditions leading to high amounts of MN component will display better hydrolytic stability.

3.3. Discussion and interpretation of MCR results

3.3.1. Effects of sample morphology on isothermal measurement

The mobility of functional groups within the resin, the diffusion rate of liberated volatiles and the sample morphology have significant effects on the ongoing processes and the chemical reactions taking place in the resin network.

With experiments under isothermal conditions vitrification effects have to be considered. If the reaction is performed below Tg, the curing reaction cannot proceed completely, as the system vitrifies and the reaction will stop at a conversion below 100% 26,27. For the investigated system, this might also have a significant influence on network composition and reaction mechanisms. The vitrification of MF resins under isothermal conditions depending on the temperature was also seen with performed isothermal DSC measurements. In a different study [28] MF resins were investigated with torsional substrate analysis at different temperatures. No information on the melamine to formaldehyde ratio was given and an unknown catalyst was used. Nonetheless, the study showed that vitrification of this resin system occurred after 40 min at curing temperatures of 115 °C but at higher temperatures, this time is significantly reduced. At 140 °C the system vitrified after 10 min and at 160 °C after 5 min.

Differences in the rheological behavior of the samples might also influence the reactions occurring in the network. The resin behaves differently at lower temperatures of 120 and 130 °C compared to higher temperatures. The powder does not soften the same way the samples at higher temperatures do. This was observed during the IR measurements,

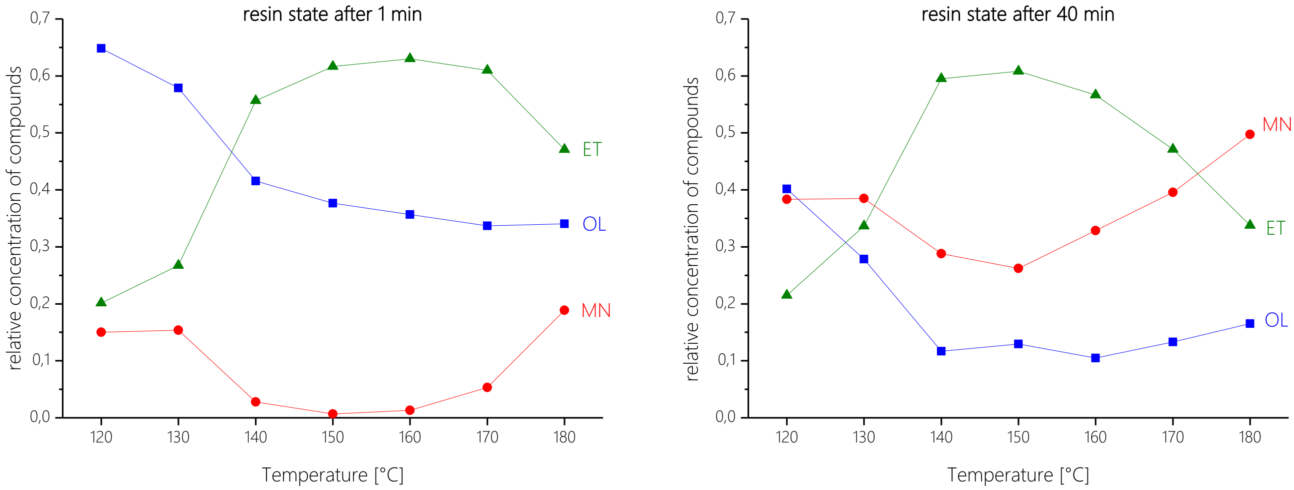

Fig. 4. Comparison of component concentrations after 1 min (final resin state for short-cycle press) and after 40 min (final state for long-term pressing) reaction time for each temperature.

as no transparent homogenous resin film is formed at measurements below 140 °C.

The IR concentration profiles over time (see Fig. 3) show that most of the reaction proceeds in a very brief time window. In this reaction phase a high degree of mobility needs to be possible within the resin network. At higher temperatures this phase is considerably shorter (<10 min) than at lower temperatures (>10 min). After that, the system is increasingly immobilized and the reaction rate finally levels off.

This phenomenon can also be seen in isothermal DEA measurements of impregnated paper sensors (data not shown here, compare the analysis presented in Ref. [24]). The measurements show that the ion viscosity increases strongly after about 10 min at 170 °C but at 120 °C, it slowly starts to increase only after 20 min reaction time. The increasing immobilization of the network is also supported by a rough estimation of the activation energy at the beginning and at the end of the reaction where an approximation of a first order reaction was performed. The activation energy at the beginning of the reaction (around 50 kJ mol^{-1}) is lower than at the end of the reaction (around 100 kJ mol^{-1}). The pre-exponential factor is lower at the end of the reaction compared to the initial value. This indicates that the activation energy depends on the extent of curing and that the mobility of the functional groups decreases with increasing network formation. This is to be assumed for multistep and condensed-phase kinetics as the properties of the sample and the reaction mechanism often depend on conversion degree and temperature [26].

Generally, it can be expected that water and formaldehyde liberated during the reaction are highly mobile within the hardening network and are entrapped in the system to a certain extent as the resin is pressed onto the ATR accessory. Hence, even if the resin is already solidified and cross-linked to a certain extent, reactions in the vicinity of reactive groups are still possible which leads to a further increase in network density.

3.3.2. *Interpretation of reaction course*

3.3.2.1. The concept of network components. The above results in Fig. 4 show clearly that all three components are present in the reaction mixture at any time during the curing reaction. The predominant species in the starting material are methylol functionalities. However, they are still present at the end of the reaction to a considerable amount. The presence of methylol compounds in “fully cured” resin samples has already been observed in previous studies [18,24]. Methylene-ether bonds are the main species that have formed at intermediate temperatures. Methylene bridges are dominant at the end of the reaction and are formed from methylol-moities as well as from the transformation of methylene-ether moieties. The reaction pathways depend on the applied curing temperature.

3.3.2.2. Low curing temperatures – 120 and 130 °C. The relative distribution of the network components (see Fig. 4) at 120 and 130 °C show a higher proportion of OL entity and hence, a lower amount of bridged species. The amount of the MN network is unexpectedly high. In contrast to higher temperatures, a significant amount of methylene bridges is present at 120 °C already at the start of the reaction. The relative amount of MN bridges initially present depends strongly on the employed M:F-ratio during resin pre-polymer preparation [29]. Fig. 3 shows that the MN concentration increases slowly but continuously during the entire reaction course. Samples at higher curing temperatures show a significant decrease of the MN component already at the beginning of data acquisition. This decrease of the MN component at certain conditions during cure under a dynamic temperature profile was already discussed in detail in a previous publication and might be due to hydrolysis reactions [24]. However, under isothermal conditions in this low temperature regime, this phenomenon is not observed. This might be due to the sample morphology mentioned above. The samples cured at 120 and 130 °C do not form a homogeneous resin film which suggests that the powder resin does not soften under these conditions. This might have an influence on the processes and reactions taking place in the sample and the resulting component concentration ratios.

Methylene-ether bonds are formed at the beginning of the reaction from methylols and decrease again throughout the reaction course. The decrease of methylene-ether moieties takes place at the same time the MN network increases which suggests a transformation of methylene-ether bridges into methylene bridges.

3.3.2.3. Intermediate curing temperatures – 140 to 160 °C. In the mid-temperature regime (140–160 °C), a considerable amount of the ET network is formed at the beginning of the reaction. The amount of MN is considerably lower compared to the experiments performed at 120 and 130 °C at the beginning of the reaction, as clearly depicted in Fig. 4. The decrease of the MN component was also described in the previous study [24] and, in contrast to the low temperature regime, a homogenous resin film is formed during the reaction. In the corresponding kinetic profiles (Fig. 3), a constant value of all compounds is reached after about 20 min (more or less, depending on the temperature). ET is the predominant spectral pattern occurring from 140 to 160 °C at the end of the reaction. In the previous study where the condensation reaction was monitored over a dynamic temperature range, the ET component is also predominant within this intermediate temperature range [24,25].

At temperatures above 160 °C, the increase of the MN compound becomes dominant in the system. Its formation is accompanied by the decrease of the ET component because methylene-ether bridges are transformed into methylene bonds (as already described in detail in a previous study [24].

3.3.2.4. High curing temperatures – 170 and 180 °C. With the reactions at 170 and 180 °C, the ET network was formed already within the first minute of data acquisition and decreases again in the following reaction course, as seen in Fig. 3. The decrease of the OL component leads to the formation of both, MN and ET moieties. The constant reaction phase is developed fast. Methylene bridges increase strongly compared to the reactions at lower temperatures which is also in agreement with the results of the previous study [24].

Due to the described difficulties such as vitrification effects and fast immobilization of the network during isothermal curing conditions, differences in the total ratios of the three network types OL, ET and MN have to be expected in comparison to reaction under dynamic heating profiles. However, in general, the results of this study are well comparable to the results of the previous studies [24,25].

3.4. *Reference to the industry and benefits of the study for future production*

Despite the difficulties of isothermal experiments and the simplifications related to using model solid resins instead of impregnated paper sheets, the presented investigations are important from an industrial point of view, as the curing process in the hot press usually is performed at isothermal conditions. The reaction conditions have a major influence on the resin properties and network formation. The chemical network composition, in turn, further influences the final properties of the produced laminates, as was shown recently in previous studies [25].

The method described here allows the quantitative determination of the chemical composition over the entire reaction course under isothermal curing conditions. In principle, the transformation of the network types into each other are the same at all curing temperatures. All experiments show similar spectral patterns that can be interpreted and assigned to certain network types that are characterized by particularly frequently occurring functional groups.

The concentration ratios of the individual components, however, differ considerably. For short-cycle pressing steps at high temperatures of 170–190 °C the network composition strongly depends on the applied temperature. It can be expected that there is a considerable difference of the network composition depending on the temperature despite the short processing times.

Increasing the temperature from 170 to 180 °C already had a significant effect on the ET to MN ratio.

For long-term pressing cycles, a temperature range from 150 ± 10 °C does not lead to strong differences of the component concentrations. The reaction has enough time to arrive at a constant phase which is similar for all experiments in this intermediate temperature range. However, for fine-tuning of the final resin properties or with regard to processing costs, the above method provides potential for optimization strategies.

The results are valid for the investigated resin system. In industry, the chemical composition of the applied resins further depends on the used M:F ratio and the applied time-temperature program during resin synthesis and the drying steps of impregnated paper sheets. These parameters are not the subject of consideration in this study but were addressed briefly in Ref. [24]. In a previous study, the influence of synthesis conditions on the resulting pre-polymer was investigated [29].

4. Conclusions

The presented method allows monitoring the kinetic profiles of different chemical components during the curing reaction of MF resins from FTIR spectra. MCR enables the separation of complex FTIR spectra into individual components that can be assigned to certain network types with typical chemical functionalities. In doing so, three components were determined which correspond to structures with predominantly methylol, methylene-ether or methylene functionalities. This allowed the prediction of the chemical composition during resin cure at defined time and temperature settings.

By using multivariate deconvolution of infrared spectral time courses, valuable results were obtained without a priori assumptions on the curing mechanism of the resin system. This allows the easy characterization and comparison of different resin samples. For industrial applications, this is highly valuable to compare different resin batches and to react quickly to e.g. resin recipe changes. For the investigation of different pressing parameters, the method possesses several advantages. Different time- and temperature settings and pressing conditions can be applied in order to work on the optimization of process parameters. This is possible for short-cycle as well as for long-term pressing programs. As the properties of the final resin surface also depend on the chemical composition of the resin network, different property profiles depending on the reaction conditions can be predicted.

In order to transfer the presented lab results to industrial conditions, further studies are required such as the inclusion of paper substrates in the curing experiments. However, the method based on FTIR/MCR presented here can serve as a basis to take these next steps on the way to implement functionality design in curing protocols.

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