Drying and Curing Behaviour of Melamine Formaldehyde Resin Impregnated Papers

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ABSTRACT: Melamine formaldehyde (MF) resins are widely used for the gluing and surface coating of wood-based consumer products in the interior design of living environments. MF resins are especially relevant in decorative laminate applications because of their good performance-to-price ratio. In their industrial processing, an important intermediate state is the liquid MF prepolymer that is used for decorative paper impregnation. Here, the drying of impregnated papers is investigated with respect to premature curing. A new method to quantify water release upon drying that allows estimation of the degree of undesired precuring is described. Since curing proceeds via polycondensation, crosslinking brings about the release of water molecules. By thermogravimetric analysis (TGA), drying was studied in terms of water release due to physical drying (elimination of "dilution water") and chemical crosslinking of the prepolymer to a three-dimensional MF network (elimination of chemically liberated water). The results obtained by TGA/IR spectroscopic analysis of the liberated volatiles show that the emission of water from b-stage MF can be clearly analytically separated into a physical (evaporation of dilution water) and a chemical (liberation via condensation) sequence. TGA experiments were correlated with curing experiments performed with differential scanning calorimetry (DSC) to estimate the residual crosslinking capacities of the impregnated papers. The drying conditions used during the preparation of impregnated decorative papers seemed to significantly affect their remaining reactivity only when harsh drying conditions were used. Upon heat exposure for prolonged time, precuring of the oligomer units results in a shift of the temperature maxima in TGA. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39860.

INTRODUCTION

Thermosetting melamine formaldehyde (MF) resins have been used for decades as finishing materials for high-quality surface applications and as binder materials for engineered wood products; their chemistry has been intensively studied.[1–12] The basic chemical reactions involved in formation and condensation of MF resins are summarized in Scheme 1. In the first step, depending on the reaction conditions (mainly the melamine-to-formaldehyde molar ratio) up to six molecules of formaldehyde may react with melamine to form primary still water-soluble methylolated melamine compounds, also known as methylols (methylolation).[13,14] These methylols may further condense under liberation of water to form the MF prepolymers,[15] which consist of either methylene- or methylene ether-bridged melamine rings. Typically, MF resin prepolymers intended for paper impregnation are of low-molecular weight and consist of a

statistical mixture of oligomers with about three to five melamine units to keep the viscosity low and allow for good paper penetration.[7] They contain usually rather high contents of methylol groups which render them reactive and allows for their rapid crosslinking when the actual laminates are formed from the impregnated papers in the hot press. In Scheme 1, a simplified oligomer is depicted showing the characteristic features of an MF prepolymer used for paper impregnation, such as low molecular weight, high methylol content, and different types of chemical bridges.

Due to the outstanding chemical and physical resistance of the cured polymer, MF fulfils the performance requirements for both low pressure laminates (LPLs) and high pressure laminates (HPLs).[16–18] The MF-based surfaces vary from high gloss to matt appearances, as well as from wood-like decorative patterns to arbitrary decors developed by designers according to modern
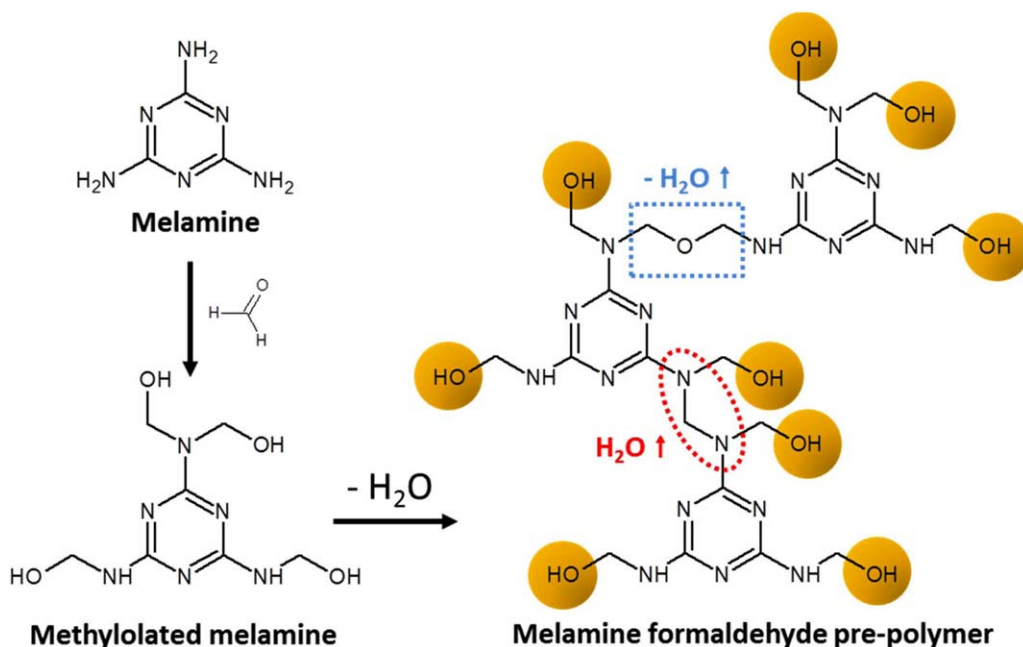
Scheme 1. Illustration of melamine formaldehyde resin formation. After methylolation of melamine further condensation of the methylolated melamines under liberation of water takes place to yield either methylene ether (marked with blue square) or methylene (marked with red circle) bridges. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

market trends. Attempts have been made to apply instrumental analysis techniques to monitor and control the composition and quality of MF-impregnated papers at various stages of production. For instance, optical spectroscopic methods have been used to characterize aminoplast synthesis[4,19] as well as the impregnation and drying process.[20] Among the thermal methods, mainly differential scanning calorimetry (DSC) has been used to model the laminates manufacturing.[21,22]

In the surface finishing of papers for decorative laminates, after an aqueous dispersion of this liquid prepolymer is applied onto the substrate, the impregnated and coated paper is dried and the solvent water is evaporated. Ideally, this drying takes place without a significant extent of crosslinking to maintain the self-gluing ability of the impregnated paper sheet. In the state of dry b-stage impregnated papers can be shipped and stored until in the final step the MF prepolymer is cured by acid catalysis to form the decorative laminate.

In order to fulfil the high standards in the optical appearance and technological performance of the final laminate, among many other technical parameters, producers of MF impregnated papers must guarantee that the produced semifinished paper sheets remain in the b stage for at least several weeks up to several months during storage and transportation. Extensive cross-linkage of MF at this stage is undesired because it deteriorates the self-gluing ability of the impregnated paper sheets during lamination. Hence, to understand what happens in the dryers after resin application is of crucial importance for controlling the quality of the produced impregnated paper sheets.

An important quality estimate used by the industry to characterize dried semifinished paper sheets is the amount of volatiles in the impregnated film which is dominated mainly by the

moisture content. If the moisture content is too high the stacked or rolled sheets are often found to stick together (block formation). On the other hand, if the content is too low the resin often has lost too much reactivity in the course of impregnation and drying already so that it will not show sufficient adhesion when finally laminated onto the carrier board. In both cases, the resin does not allow forming surfaces that fulfil the customer's requirements.

For quality control, simple and efficient ways for monitoring the volatile content (VC) of b-stage MF resins and predicting the reactivity are, therefore, of great importance. The weight loss of manufactured impregnated papers upon drying (usually performed for 5 minutes at 165°C in a drying chamber) indicates the remaining VC of impregnated paper. In the industry, this information is qualitatively used to estimate the technical performance of the product. Usually, when the dried paper contains residual moisture in a range between 5% and 7% VC, the storability and the resin flow during the pressing step is found to be satisfactory.

However, this technological test does not distinguish between the amount of water that has been present as the solvent from the beginning (MF oligomer dispersions are typically employed as aqueous systems that contain about 50–60% dry mass!) and the additional amount of water that originates from crosslinking during the chemical step of curing. Hence, no detailed quantitative information can be deduced regarding the established degree of crosslinking upon drying and the resulting remaining self-gluing ability.

Despite this lack of knowledge about the actual curing state of the resin after passing the dryer, it is still often tentatively assumed that the drying conditions will have a major effect on

the further processability of b-stage impregnated paper regarding the blocking behaviour, the storage stability, the self-gluing ability, and the delamination tendency by influencing the precondensation degree and the crosslinking state of the MF. In practice, it is basically assumed that too harshly dried papers of low VC should feature highly precured MF states that in turn should yield, for instance, a low self-gluing ability during hot pressing and a high delamination tendency of the manufactured good.

In this study, the experimental basis for these industrial premonitions is more closely studied by using thermochemical methods, and a more precise method for indirectly monitoring the precondensation degree during impregnated paper processing while still being not too sophisticated for a typical industrial environment is suggested.

For an improved process control, it should be important to know about the relative contributions of the portions of dilution water and condensation water evaporated during drying. In the industrial process, during the necessary drying of the paper it is aimed at eliminating mostly the dilution water without significantly altering the precondensation degree of the resin, that is, without generating significant amounts of water molecules due to undesirably high degrees of curing progression. Hence, it is hypothesized in this study that by being able to analytically distinguish between the amount of solvent water evaporated and the amount of water liberated during condensation, a deeper understanding of the precondensation processes taking place during the drying of MF impregnated paper would be gained which in turn would allow for much improved process control of the manufacturing process.

To this end, the drying and curing behaviour of impregnated paper sheets containing b-stage MF resin was analyzed by instrumental thermal analysis methods in order to better understand the processes taking place during drying of impregnated decorative papers. The major aim was to evaluate whether by using thermogravimetric analysis coupled with infrared spectroscopy (TGA-IRS) the volatiles liberated from b-stage MF during a variety of drying conditions can be analytically separated into a physical and a chemical sequence of water emission. Based on the comparison of TGA-IRS analysis with curing experiments performed with DSC analysis of corresponding paper samples, the influence of the drying conditions on the remaining crosslinking ability of b-stage decorative paper sheets are discussed.

EXPERIMENTAL

Chemicals
Melamine (99%), formaldehyde (36.8 wt % in H_2O), HCl (10%), NaOH (20%), formic acid (88%), and sulfamic acid (99.3%) were used as received by Sigma-Aldrich Handels GmbH Vienna.

Prepolymer Synthesis
MF precondensate was synthesized similar to the procedure described earlier.[1,2] The M:F ratio was 1:1.9. The reaction temperature was kept between 92°C and 94°C. The resin was condensed until a water tolerance of 250% (v/v) at a resin

temperature of 20°C was observed which was the case after a reaction time of approximately 90 min. Thereafter, the precondensate was cooled to room temperature. For assaying water tolerance, 5 mL aliquots of the resin were transferred into a test tube and metered amounts of distilled water were added using an automatic titration system until the resin dispersion became cloudy. The volume percentage of added water first causing a permanently white dispersion (due to the precipitated resin) equalled the water tolerance. The prepolymer had a solid content of 55.1% (w/w). To prevent unexpected side effects, no auxiliary processing agents such as wetting agent were used. As only additive, an acid catalyst for accelerating the curing,[2] a 1% (w/w) aqueous solution of sulfamic acid was freshly prepared and added.

Paper Raw Material
As the substrate for impregnation, a special decorative paper, the so-called overlay was chosen (MD Papeis, Barcelona, Spain). Overlay paper consists of pure α-cellulose fiber with minor traces of chemical additives such as binders. Upon impregnation with MF and hot pressing onto a carrier, the paper becomes completely transparent. This kind of paper is used in the flooring industry together with corundum-filled MF resins in order to apply a protective abrasion- and microscratch-resistant layer on top of the decorative layer. The used paper had a grammage of 28 g m^{-2}.

Paper Impregnation
For paper impregnation on a laboratory scale, suitable overlay paper sheets of 30 cm × 30 cm were cut and dipped into the prepared MF resin for 5 seconds. After this time, the impregnated paper was pulled through two rollers to remove excessive resin. The impregnation was repeated 3 times for every test specimen. After removing excess resin, the wet paper was placed and fixed by magnets onto a drying frame and dried for defined time periods. All papers were impregnated with a resin load of 80 g m^{-2} MF resin.

Paper Drying
Laboratory-scale simulation of the industrial drying was done in a Mathis LTE lab Dryer (Mathis, Germany) equipped with an inline infrared sensor to determine the surface film temperature. The oven was operated at a constant temperature of 130°C with a fan set at 2300 rotations per minute. Heating was performed with an electric capacity of 2400 Watts. Immediately after fixation on the frame, the paper was exposed to the drying temperature for different drying times, D_t (D_t = 30, 40, 50, 60, 70, 80, 80, 90, 100, 110, and 120 seconds) in the Mathis Oven. Due to the special construction of a narrow sample entrance slit that allows introduction of the material to be dried without the need of opening an oven door, the oven temperature did not change significantly upon introduction of the sample into the heating chamber. Hence, all samples experienced the same temperature level from the very first second. The wide range of temperature–time profiles used for the laboratory-scale drying experiments in this study extends well beyond the potentially expectable heat treatments industrially manufactured impregnated papers usually experience during the production-scale drying processes. For comparison, assuming an actual

processing speed of, for instance, approximately 60 m min^{-1}, an impregnated paper that is manufactured on an industrial dryer line of, for instance, 40 m length is subjected to the heat in the dryer at the most for about 40 seconds at the average drier temperature used.

DSC analysis

Thermograms were recorded on a Mettler-Toledo (Greifensee, Switzerland) 822e differential scanning calorimeter at a temperature range from 25°C to 200°C, and a heating rate of 10°C min^{-1}. All experiments were performed in HD crucibles in order to prevent the evaporation of water.

TGA with IR Coupling

A TA Instruments TGA Q5000 (TA Instruments, USA) with IR coupling was used. The IR coupling was used to characterize the chemical functionality of the volatile emissions during the experiments. The temperature range was 25–200°C with a heating rate of 10°C min^{-1}. Samples of 4 mg were weighted in. Measurement results were corrected by accounting for the actually used weight. All measurements were performed in platinum vessels. As flow medium, nitrogen gas was used with a flow rate of 25 mL min^{-1}.

Gravimetric VC Determination

As a reference method, gravimetric determination of the VC in the dried impregnated papers was performed according to the protocol that is generally applied in current industrial process control. Circular samples with a diameter of 10 cm were cut from the dried impregnated papers and further dried in a conventional drying chamber at 165°C for 5 minutes. The weight loss brought about by this second drying step was determined gravimetrically by comparing the paper weights of the samples before and after the second temperature treatment.

RESULTS AND DISCUSSION

To study the influence of the drying conditions on the curing state of the MF resin present in the dried paper samples, a series of impregnated papers were prepared and dried at 130°C for different time intervals. All papers were analyzed by TGA-IR and DSC after drying. For comparison, the weight loss of the impregnated papers was determined also by the conventional technological method routinely used in the industry.

Effect of Drying Conditions on Volatile Emission During Drying

The effect of drying conditions on the emission of volatiles during the drying process was studied by thermogravimetry. The TGA thermograms for all dried impregnated paper samples are shown in Figure 1. Table I summarizes all relevant characteristics of the studied impregnated papers such as the drying conditions (applied drying times and measured film surface temperatures that were observed during the drying), the paper weights used for the moisture content calculations, the peak integrals of the maxima in weight loss that were observed in the TGA experiments as well as the characteristic features of the DSC traces of the impregnated papers (onset and end-set temperatures as well as normalized peak integrals).
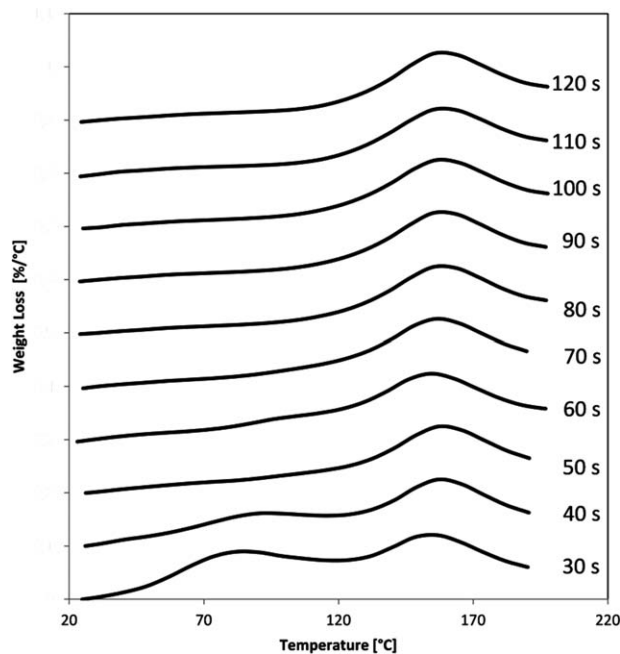
Figure 1. Thermograms obtained from TGA experiments with impregnated paper samples that were dried at 130°C for different time periods. All samples contained 80 g m^{-2} MF resin.

Figure 1 shows that the weight loss of a typical impregnated paper sample takes place in either one or two steps depending on the applied drying time. With the samples dried for longer periods (>60 seconds) at elevated temperature, only one distinct peak in weight loss is observed in the thermograms at around 150°C. In contrast, the samples that were subjected only to a short heat treatment (<60 seconds) displayed two weight loss peaks, the first of which appearing at around 85 °C, and the second peak appearing again at about 150°C. This indicates that the drying conditions had a significant effect on the chemistry of the impregnated papers. To characterize the nature of the volatile compounds evaporated from the harshly and the moderately dried impregnated papers, infrared spectroscopy was performed on the gaseous phase liberated during the TGA experiments.

Figure 2(a,b) shows two typical infrared spectra obtained from the evaporated species at the respective weight loss peaks. Figure 2(a) shows the IR spectrum of the compound eliminated during the first peak maximum, Figure 2(b) shows the IR spectrum of the compound eliminated during the second peak maximum. Obviously, both spectra are identical and represent the same volatile compound which was identified as water vapour and traces of carbon dioxide. Hence, it was concluded that both observed TGA peaks resulted from the evaporation of water from the impregnated paper samples.

Since the temperature maximum of the first peak in weight loss due to water evaporation was found well within the region of the boiling point of water, it was attributed to the elimination of residual water originating from the dilution water present in the used aqueous dispersion of the impregnation resin formulation. To be sure that this assumption was correct, a blank

Table I. Summary of Predried Impregnated Paper Characteristics as Determined Using the Conventional Gravimetric Final Moisture Content, Thermogravimetry, and Differential Scanning Calorimetry

Exp.	D_t (seconds.)	P_w (g m^{-2})	R_w (g m^{-2})	R_u (%)	S_t (°C)	VC (%)	$E_{1st\ peak}$ (%)	$E_{2nd\ peak}$ (%)	OS (°C)	ES (°C)	NI (J g^{-1})
1[a]	120	0.304	n.d.	n.d.	100	n.d.	4.01	0.00	n.d.	n.d.	n.d.
2	30	0.295	0.89	302	90	10.6	5.07	7.07	118.18	169.46	22.88
3	40	0.297	0.773	260	98	8.1	3.43	7.12	117.73	174.23	20.48
4	50	0.304	0.892	294	103	6.8	2.19	6.98	118.33	184.52	33.44
5	60	0.276	0. .73	265	106	6.7	1.94	6.86	118.29	183.68	37.45
6	70	0.289	0.817	283	107	6.3	1.66	6.82	118.28	185.58	n.d.
7	80	0.278	0.718	259	107	5.6	1.30	6.78	118.18	191.34	27.84
8	90	0.274	0.787	288	107	5.5	1.23	6.86	118.01	184.91	n.d.
9	100	0.293	0.823	281	108	5.5	1.21	6.86	118.39	185.21	37.88
10	110	0.282	0.843	299	108	5.1	1.14	6.79	118.31	180.48	22.68
11	120	0.269	0.737	274	108	4.9	1.07	6.65	118.02	177.22	33.16

D_t, drying time; P_w, weight of the raw overlay paper; R_w, weight in dry condition; C, amount of resin absorbed; S_t, surface temperature during drying; VC, volatile content as determined by the conventional method (drying at 165°C for 5 minutes); $E_{1st\ peak}$, emission of H_2O during peak one (evaporation of solvent) between 30°C and 118.44°C; $E_{2nd\ peak}$, emission of H_2O from the condensation reaction between 118.44°C and 200°C; ON, onset of the resin curing in DSC measurements; ES, endset of the resin curing in DSC measurements; NI, normalized integral.
[a] Experiment 1 was a blank experiment where the impregnation of paper was carried out with pure water without any resin in order to validate the first water evaporation peak found in TGA.

experiment was performed where overlay paper was impregnated with pure distilled water. After applying the drying procedure (120 seconds at 130°C) thermogravimetry was done. Only one evaporation peak was found in the thermogram which corresponded well with the first TGA maxima found with the resin impregnated papers (see entry 1 in Table I).

The second water evaporation maximum appeared at a much higher temperature at about 150–160°C when the dilution water was practically already completely eliminated. Hence, it was concluded that this second peak represented the amount of water liberated by the condensation reaction during crosslinking of the MF resin at elevated temperatures. The temperature range of this second peak corresponds well with the processing temperatures that are typically employed in the hot pressing of MF-

based products and assigning it to the chemical curing reaction is hence reasonable.

The impregnated papers that were dried under very mild conditions, that is, using very short drying times in the drying experiments, displayed both distinct water evaporation steps in the TGA thermograms. This indicates that moderately dried papers contain significant (and quantifiable) amounts of the dilution water from the original resin formulation (first peak) and do still show residual curing ability during the TGA experiment as indicated by the second peak maximum in the TGA thermogram.

No such first evaporation step was observed with the samples dried at very long drying times. While with the sample dried for 40 seconds at 130°C still some residual moisture was removed during the TGA experiment, no such water evaporation at all occurred with the samples subjected to drying times >60 seconds. This is indicative for an increasingly complete removal of the dilution water, that is, drying of the impregnated papers with increasing drying times.

It should be noted that by analyzing the MF impregnated papers by TGA, obviously a clear analytical separation of the water evaporated during the crosslinking reaction ("condensation water") and the water evaporated from the solution ("dilution water") can be achieved. This opens up the possibility to use thermogravimetry as a powerful tool to quantify exactly both the amount of residual water and the condensation degree obtained upon paper processing. Since for each molecule water that is liberated during condensation one methylene or methylene ether bridge is formed in the three-dimensional polymer network, TGA in principle delivers a direct method for determining the crosslinking density of partly or fully cured MF products.
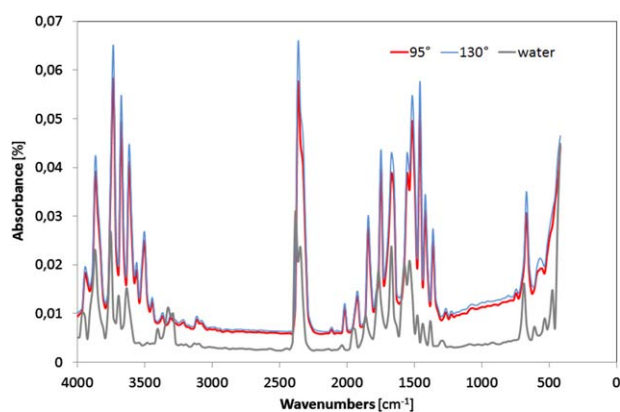
Figure 2. Online IR Spectra of the volatile emission recorded during the TGA experiment (left: first peak, appearing in the temperature range 30–118°C; right: second peak appearing in the temperature range from 119–200°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

According to the original hypothesis of the present study, the drying procedure should exert a significant impact on the precondensation degree of impregnated papers and hence, should strongly influence their remaining self-gluing properties. Accordingly, in the most harshly dried paper samples used in the present study, the curing should have taken place already completely or at least to a great extent during the drying procedure and no or only a minor residual curing reaction should be observable when subjecting the dried paper to the heat gradient in the TGA experiment. Since such residual curing would be indicated in TGA by a concomitant release of water due to the condensation reaction, papers containing MF with already a high degree of precondensation should show a much reduced or no water evaporation step at all in the TGA thermogram at high temperatures due to the already largely finished crosslinking reaction.

In contrast to this, it was found that all papers, even those subjected to the longest drying times displayed a high temperature water evaporation maximum for all samples, mildly and harshly dried ones, no matter how they were dried prior to the TGA experiment. However, the temperature at which the maximum in weight loss appeared shifted with increasing heat load slightly towards higher temperatures from about 154°C (with the samples dried for 30–50 seconds) to nearly 159°C (with the samples heated for >100 seconds).

Hence, it can safely be concluded that not even drying the impregnated papers under the most severe of the conditions tested here (which were drying for 2 minutes at 130°C, which represents a temperature–time profile that is probably never reached under real process conditions!) may leave the impregnated paper completely "dead", that is, having totally lost its self-gluing ability. On the contrary, the predried papers investigated in the present study did, if at all, show only marginal and statistically not significant changes in their remaining reactivity as indicated by the second water emission peak (see Table I and Figure 4) and the DSC integrals (see Table I). This is a very interesting result that has important implications for the industrial processing of impregnated paper sheets.

Effect of Paper Matrix on Drying and Curing Behaviour of MF Resin

For a rough estimation whether the drying and curing behaviour of liquid MF resin was significantly distorted by the used overlay paper matrix, the TGA of a neat liquid resin sample was also performed for comparison. The liquid resin sample was dried for 70 seconds at 130°C first in order to account for a typical drying step. The corresponding TGA thermogram (data not shown) displayed two characteristic peaks occurring in similar temperature regions as observed in the TGA thermograms obtained with the impregnated papers. Whereas the value for the second peak maximum which was attributed to the curing reaction occurred again at about 160°C, the first peak maximum due to the evaporation of dilution water was found at a slightly lower temperature (70–72°C). Hence, it was concluded that whereas the evaporation of dilution water is somewhat easier when no paper matrix is present, no significant influence of the overlay paper on the actual curing behaviour in terms of
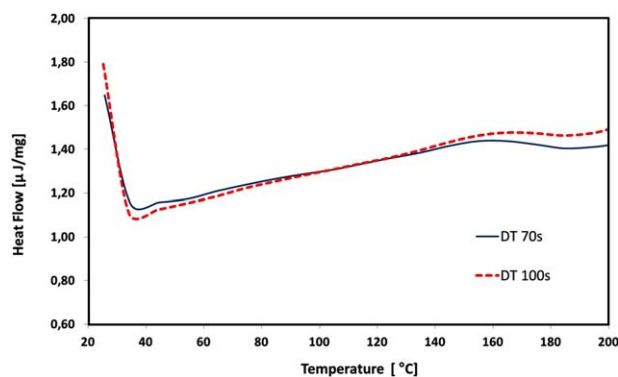
Figure 3. Differential scanning calorimetry thermograms of representative paper samples predried at 130°C for 70 (DT 70s) and 100 (DT 100s) seconds. The experimental error was calculated from three replicate runs performed on the paper sample predried for 100 seconds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

temperature shifts in the TGA could be detected in the present system. However, since the used overlay paper practically consists of pure α-cellulose and does not contain any additives, the situation may be different with other types of paper used in decorative laminates.

Effect of Drying Conditions on Residual Reactivity of Impregnated Papers

In the next step, the residual reactivity of the impregnated papers as a measure for their remaining self-glueability and, in turn, processability in hot lamination, was studied with DSC.

Figure 3 shows two typical thermograms from DSC measurements of predried impregnated paper and Table I summarizes the characteristic values of all thermograms for the differently dried paper samples (on-set temperature of the resin cure, end-set temperature of the resin cure, normalized peak integral of the curing enthalpy).

In Figure 3, the experimental error in determining the DSC thermograms is also given to illustrate the difficulties in obtaining statistically significant results with this method. The standard deviation of the single measurements was quite high and the integrals of the curing peaks were rather difficult to determine accurately and reproducibly. The reason for these experimental uncertainties is that in measuring impregnated paper samples with DSC, the obtained signals are rather low. Impregnated paper samples display rather low and varying degrees of resin content on a microscale and, hence, DSC measurements are much less reliable than when neat liquid resins are analysed. Even more problematic, predried impregnated paper samples are not ideally flat which hampers good contact of the sample with the bottom of the measurement crucible. This leads to imperfect heat transfer during the experiment and, hence, to larger deviations of thermograms between repeated samples. Therefore, the determination of the remaining reactivity towards curing of predried paper samples is rather tainted with experimental error and the values for the peak integrals given in Table I merely demonstrate that within the analysed set of differently
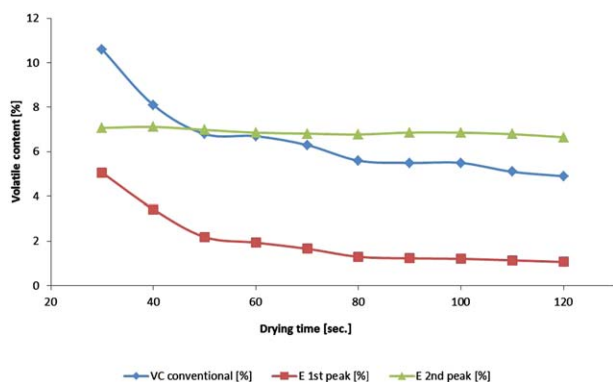
Figure 4. Comparison of the values for evaporated volatiles (basically water) from impregnated paper samples that were predried for different time periods as determined by the conventional testing method (diamonds) and by thermogravimetry (squares: integral of the first evaporation peak, E_1st $_{peak}$; triangles: integral of the second evaporation, $E_{2nd\ peak}$). In the conventional testing method, the predried impregnated paper samples are further subjected to a temperature of 165°C for 5 minutes and the total amount of volatiles is determined gravimetrically. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dried impregnated papers no statistically significant differences in the remaining reactivity could be detected.

Nevertheless, with all samples, even the most harshly dried ones, significant exothermic peaks were observed, and hence, all predried papers displayed still good chemical reactivity.

Moreover, the temperature range within which the main exothermy took place correlated well with the temperature at which the second peak maximum in the thermogravimetry experiments occurred. Curing of the prepolymer typically takes off at a temperature of about 118°C (on-set temperature) and the highest activity of curing was found between 152°C and 155°C, independent of the applied drying times.

One possible reason for the little influence of the drying procedure on the remaining curing reactivity of dried papers might be a combination of the relatively low film temperatures that are achieved during the drying (see Table I) and the reduction in reactivity of the prepolymers by the removal of the solvent water.

The film surface temperature is relatively low for all predried paper samples and ranges from less than 100°C with the mildly dried papers to at the most 108°C with the most harshly dried ones. From the curing progression seen in the DSC thermograms it is evident that the crosslinking reaction requires higher temperatures to proceed with significant reaction rates. Hence, even under the most severe drying conditions in the studied experimental series the offset temperatures for crosslinking had not yet been reached.

Furthermore, as evident from Figure 4, practically no more solvent water is present after longer periods of drying that is physically evaporated. In such a dry state the acid catalysed polycondensation reaction is thought to be very slow because the large molecules have a low mobility due to diffusion limitation

and the probability of molecular interactions that lead to a chemical reaction is rather low. This might also contribute to the surprisingly low influence of the drying conditions on the remaining curing reaction.

Comparison of TGA with Conventional Gravimetric Residual Moisture Assay

TGA offers a more detailed and accurate view of the volatile emission during drying than does the conventional gravimetric method. This is illustrated by Figure 4.

Figure 4 features the amounts of evaporated water during the TGA experiments (in terms of integrals of the first (squares) and the second (triangles) peak in the TGA thermogram) for the samples predried at 130°C at different drying times (30–120 seconds). These values are compared to the experimental values for the volatile determination obtained with the conventional procedure of heating representative weight equivalents of the impregnated paper after the defined predrying step for further 5 minutes at 165°C. The latter method is used as the standard testing method in the industry for process monitoring of the residual moisture content of the paper. The paper is weighed before and after this additional heating phase and the total amount of volatiles evaporated during the heat treatment is determined as the weight difference, usually expressed as percentage in relation to the weight of the predried paper.

The values obtained with the conventional gravimetric method show that increasingly less amounts of volatiles are released from the impregnated papers the longer they are dried. This is the same trend as is observed with the first peak in the thermogravimetric experiment and corresponds well to the removal of dilution water from drying. The integral of the second evaporation peak in TGA (triangles in Figure 4), in contrast, is not very much influenced by the intensity of drying. Hence, the drying conditions employed in this study, although covering a wide range of heating profiles, yielded, if at all, only a minor alteration of the precondensation degree of the resin prepolymer.

It is obvious, that the standard method used in industry determines both the evaporated solvent water and the water liberated by the condensation reaction. Hence, by using this testing procedure it has never been possible so far to accurately draw reliable conclusions on the precondensation degree of the tested impregnated papers and assumptions deduced from relating the test results to the final technological performance in the subsequent hot lamination step have always been, at best, of qualitative nature.

From Figure 4 it is seen further that the conventional method does not even determine the actual sum of the relative contributions of dilution and condensation water accurately since the papers are not completely dried but only subjected to an arbitrary heating procedure that has developed historically and was seen fit for use, but has never been challenged on a scientific basis. Hence, the informative value of this testing method is even more questionable. The reason why this testing method seemed to work well in the past is that the curing state of the impregnated papers is not very much influenced by the drying process at all as indicated by the relatively stable integral of the

second water emission peak (triangles in Figure 4) that represents the remaining crosslinking ability of the impregnated paper. Since all measured values for the absolute amounts of liberated water during the curing phase were well between 6.65 and 7.12% (or 1.53×10^{-5} and 1.60×10^{-5} mol water per normalized sample weight) it can be assumed that the drying of impregnated decorative papers usually does not much influence the degree of crosslinking of MF, especially when only those values are considered that reflect most the real drying conditions under industrial conditions, that is, the rather mild conditions of 30–50 seconds exposure time used in the experiments 2, 3, and 4 (Table I). However, inspection of Table I also reveals that a slight trend towards a decrease in the second water emission peak integrals is present in the data which points to a minor reduction in crosslinking reactivity when extremely harsh drying conditions are employed (around 7% moisture liberation at 30–50 seconds drying time compared to 6.65% moisture liberation observed at 120 seconds drying time). In addition, a slight peak shift in the second TGA peak integral was observed towards higher temperatures with increasing drying times. Therefore, although the observed effects are rather small, it may not be safe to conclude that drying has never any influence on the final paper properties, especially, since the applied drying regime in an industrial plant may vary strongly for different products.

Using thermogravimetry instead of the conventional testing method offers not only good resolution of the evaporated water with respect to its origin but furthermore allows for exact quantification of the actual amounts, that is, the number of moles of water liberated per area unit, and hence, allows to deduce some general idea on the actual precondensation degree of the resin that may have developed upon harsh drying.

However, detailed information on the precondensation degree, the nature of the crosslinked network and the processing and application properties of the resulting paper sheet is not accessible by using TGA alone. Different types of chemical bridges can be formed by the condensation; from the amount of water liberated only an estimate of the total crosslinking density can be deduced. Elucidation of the exact crosslinking state of predried impregnated paper will be subject of further studies. The aim of the present study was restricted to show that TGA can be beneficially used for monitoring the removal of solvent water during the industrial drying process. By applying TGA instead of the conventional testing method it is possible to control the drying process in a way that exclusively drying takes place without initiating undesired early crosslinking to a significant extent. To recognize this practically important information is beyond the traditional way of gravimetrically determining the residual moisture content in dried papers.

Based on the findings in the present study the authors suggest to rethink the traditional way of measuring the moisture content of impregnated papers by determining the weight loss gravimetrically as a technological measure for the b-stage condition of the impregnation resin upon drying. The values measured by this method are not suitable for indirect estimation of the precondensation degree of MF resin since they do not account for ambiguities arising from slightly different resin percentages applied to the paper. Such slight variations in resin loading may easily occur in practice during the impregnation and coating processes and need to be analytically covered by the testing method. For example, rather harsh drying conditions of a paper carrying a larger amount of MF resin should yield similar values for the relative moisture content like a moderately dried paper carrying lower resin loads. However, although displaying similar values for the residual moisture content, the former paper might show inferior postprocessing properties whereas the latter may still be of sufficient quality. Hence, the conventional gravimetric method may be strongly misleading especially in cases where the processing window for the precondensation degree of the MF resin is very narrow and, hence, the drying needs to be carefully controlled. By applying instrumental analysis such as thermogravimetry it is possible to establish more reliable information on the precondensation state of the impregnation resin which in turn should lead to better control of the production process in especially critical cases.

CONCLUSION

Impregnation and drying experiments were performed on a laboratory scale by applying a water-based dispersion of MF prepolymer, mixed with an acidic curing agent, to pure cellulose overlay paper. The resin impregnated papers were dried for different times and then analysed by TGA. It was found that TGA allows clearly differentiating between the emission of water originating from the evaporation of solvent water during drying on the one hand and water formed as a product of the polycondensation reaction taking place during crosslinking of MF. Based on the findings it was concluded that during a typical process of paper impregnation under industrial conditions only evaporation of solvent water takes place as long as the applied heat load is rather low. Under such mild drying conditions the crosslinking of the prepolymer by polycondensation as indicated by the weight loss was not significantly enhanced by the drying procedure even at longer drying times at 130°C. DSC analysis, however, also showed that under increasingly harsh drying conditions the remaining reactivity and, hence, the self-gluing ability of impregnated papers is deteriorating. The thermograms showed that the drying of the prepolymer had a strong influence on the content of residual solvent in impregnated paper. It is suggested to apply the described TGA procedure as a means of quality control in industrial practice since it leads to much more detailed and conclusive information on the state of dried impregnated papers than does the conventional test method currently used.

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