Eur. J. Wood Prod. (2010) 68: 63–75
DOI 10.1007/s00107-009-0352-y

ORIGINALS · ORIGINALARBEITEN

On the performance of a melamine–urea–formaldehyde resin for decorative paper coatings

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Received: 30 September 2008 / Published online: 13 June 2009

Abstract The decorative laminates industry is a highly competitive industrial sector. To be profitable, manufacturers of impregnated papers for surface laminated MDF and particleboards need to significantly reduce their production costs. Melamine formaldehyde resin (MF) formulations are commonly used for impregnation and coating of such papers, melamine being an important, but costly raw material used in high quantities. While MF is substituted by cheaper urea formaldehyde resins (UF) in the core impregnation, for paper surface films pure MF is used. Therefore, a further reduction in cost could be achieved if a portion of the melamine in the surface film was replaced by urea. In the present contribution, recent results of technological tests on paper laminates using a novel melamine–urea–formaldehyde resin (MUF) formulation are reported and their performance is compared to traditional surfaces made from MF.

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Über die Eigenschaften eines Melamin-Harnstoff-Formaldehyd Harzes für die Dekorpapierbeschichtung

Zusammenfassung Die Dekorlaminatindustrie ist ein sehr wettbewerbsintensiver Industriesektor. Um profitabel zu sein, sind die Hersteller von imprägniertem Papier für Oberflächen von laminierten MDF und Spanplatten gezwungen, ihre Produktionskosten zu minimieren. Melamin-Formaldehyd-(MF)-Harze sind als Imprägnierharze für solche Papiere weit verbreitet und große Mengen des teuren Rohstoffs Melamin werden dabei verbraucht. Während MF in der Kernimprägnierung bereits großteils durch kostengünstigeres Harnstoffharz (UF) ersetzt wird, verwendet man für Oberflächenfilme nur MF. Daher könnten weitere Kosten gespart werden, wenn ein Teil des Melamins in der Oberfläche ebenfalls durch Harnstoff ersetzt werden würde. Im vorliegenden Beitrag wird von aktuellen technologischen Testergebnissen an Laminaten mit einem neuartigen Melamin-Harnstoff-(MUF)-Harz im Vergleich zu traditionellen MF-Oberflächenfilmen berichtet.

1 Introduction

The wood based panels industry is of tremendous economic importance. The worldwide capacity has reached 223 Mio. m^3 in 2005 which is an increase of more than 20% since the turn of the century. For the major carrier materials for coated elements in the furniture and flooring industries, particleboard (PB) and medium density fibre board

(MDF) projections from 2003 to 2007 assumed an increase from 80.9 to 87.8 Mio. m^3 (PB) and 42.2 to 55.3 Mio. m^3 (MDF), respectively (Barbu 2006). 70% of the manufactured boards are covered with resin impregnated paper sheets for decorative and protective purpose, the rest is finished with wood veneer and thermoplastic films or is painted or printed (O'Carroll 2004). Currently, Europe dominates the world market in production and consumption of such products with a volume of about 5.3 billion m^2 (O'Carroll and Goroyas 2006). However, the European market is nearly saturated and cut-throat competition between the manufacturers is very harsh leading to massive concentration of the production capacities in only a handful of big companies. Most of them are integrated producers of coated wood based panels (WBPs) which manufacture both, the impregnated paper and the carrier material for thermo-fusing. Growth can primarily be found in Eastern Europe, Latin America and Asia – China being the most dynamic area (Hogg 2004, Ye et al. 2008, 2009). For China, an annual growth of 27% in the production of MDF was observed since 2002 (Ye et al. 2008). Due to the booming domestic market, China has developed to the world's biggest producer of MDF by contributing about a third of the total world production (Ye et al. 2008) and while in 2005 190 Mio. m^2 of laminate flooring were produced this amount is projected to double by 2010 (Ye et al. 2009).

Thus, new competitors from states with rapid economic growth emerge and dramatically further increase the pressure on the market. Competition for shares in current and emerging markets is becoming increasingly aggressive and it is inevitable for a manufacturer of impregnated paper for WBP coating to minimize his production costs and increase productivity by substituting costly raw materials and increasing the material throughput.

As a first step in the production of impregnated papers, the décor paper is impregnated with resin and then predried. Here, for cost reasons, in many cases urea formaldehyde resin (UF) is used instead of the more expensive melamine formaldehyde (MF). In a second step, the impregnated paper is coated and the pre-preg is dried to a final moisture content of 6–7%. Currently MF formulations are commonly used for coating due to their unique surface properties. Cost savings by substituting a portion of melamine in MF by urea would be highly desirable and could be achieved either by mixing MF and UF or by preparing a suitable melamine–urea–formaldehyde (MUF) co-polymer. In the final hot pressing step, a suitable carrier, PB or MDF, is coated with the self-gluing impregnated paper. In both the impregnation/coating as well as the thermo-fusing steps, production speed should be as high as possible.

However, an increase in production speed often leads to a deterioration of process reliability and product quality. MF surface films must be highly durable and chemically inert. They must be easy to clean and need to display an optically attractive appearance. The formation of a smooth surface film is crucial for their application properties. For example, surface defects in finished boards such as pin-holes may be caused by an incomplete impregnation due to the chosen impregnation speed being too high. It has been described earlier that complete core impregnation of the paper is a prerequisite for the forming of a satisfactory surface film (Roberts and Evans 2005). With too high line speeds the impregnation solution may not have sufficient time to thoroughly penetrate the paper resulting in areas where the pores are not properly filled with resin. In such holes the MF coating resin sinks down during the subsequent pressing step and gives rise to local surface defects. Therefore, many different MF impregnation resins have been developed in industry in order to achieve extremely high penetration of paper according to the highest possible impregnation speed (Bader et al. 2002, Kirchgaessner and Niessner 1992). On the other hand, a reduction in pressing time required for the surface finishing of the panels with resin films during the hot pressing step is essential for minimizing production costs. Depending on product type and pressing technology the press dwelling times required for lamination range from about several minutes with multi-platen presses to as low as a few seconds with modern short cycle presses. Impregnation resins must cure sufficiently fast and defect-free film formation must readily occur to allow for the short pressing cycles.

Thus, to successfully substitute MF, MUF resin must fulfil a number of requirements. Besides good impregnation properties of the liquid resin such as low solids content, low viscosity and reasonable water tolerance, the processing properties of MUF impregnated papers must be good as well. The papers must display reasonable flexibility, sufficient flow times and a suitable degree of cross-linking. With respect to the rapid processing in short-cycle presses during lamination, papers must furthermore be highly reactive and provide smooth film formation. Finally, the board properties of MUF coated panels such as hydrolytic stability, chemical resistance, surface smoothness, cleaning ability and visual appearance must be satisfactory for the end-customer.

In summary, a MUF resin must fulfil a number of requirements in order to be able to substitute MF resins in durable decorative surface coatings. Only when the technological properties are satisfactory in comparison to conventional MF and its processability is in compliance with the manufacturing conditions, the advantage of lower raw material costs with MUF legitimates its industrial use.

In the present contribution, the applicability of a novel MUF impregnation resin is investigated with respect to its technological potential to substitute MF in the surface finishing of particleboards intended for fronts in furniture and kitchen applications. Based on the recipe for a typical MF

impregnation resin, a MUF co-polymer was prepared where 30% of the melamine was substituted by urea resulting in a reduction of raw material costs of approximately 15%. The technological performance of MUF was assessed with industrial standard tests for chemical resistance, cleaning ability and visual appearance of the resulting laminate surface by determining the acid value, porosity and gloss. The processability of the MUF impregnated papers was assessed by measuring the dynamic-mechanical properties of the impregnated papers using the Golombek testing device which is routinely used in the laminates industry.

2 Materials and methods

2.1 Materials

The decorative paper used in this study was a white design of 70 g m^{-2} typical for the application in decorative working surfaces such as in kitchen and bathroom furniture and was supplied by Munksjö Paper Decor GmbH & Co. KG, Aalen, Germany. Commercial MF for paper impregnation, impregnation additives (wetting and antifoaming agent, modifier) as well as raw materials for MUF resin preparation (melamine, urea and formaldehyde) was kindly donated by Impress Décor Austria GmbH. Different MF curing catalysts were supplied from BASF (Ludwigshafen, Germany).

2.2 Preparation of MUF

MUF resins with a melamine–urea/formaldehyde molar ratio of 1 : 1.9 and a melamine/urea weight ratio of 47 : 53 were prepared according to a modification of a known manufacturing procedure (Depres et al. 2007, Kandelbauer et al. 2007) as follows. 119.24 parts of urea, 105.76 parts of melamine and 60 parts of water were added to 442.0 parts of formalin (37%). The pH was set to 10–10.4, and the temperature was brought to 90 °C under mechanical stirring. An exothermic reaction occurred when the melamine dissolved under methylolation. After reaching the reaction temperature, the pH was lowered to 7.8 and the reaction was continued at the same temperature. During the reaction, the pH was allowed to fall down to 7.3–7.4. The water tolerance of the resin was checked every 10 min until the solubility of the resin decreased significantly. When the water tolerance (the percentage of water that could be added to the liquid resin) reached a value of 180 to 200%, the reaction mixture was cooled to room temperature. The final water tolerance at room temperature was 150%.

The reaction system was equipped with a Schott Steamline online pH electrode and PT 1000 temperature sensors (Schott AG, Mainz, Germany). The pH profiles were recorded and electronically adjusted during the reaction with a MultiT system from Jensen Systems (Hamburg, Germany). A typical reaction profile in terms of pH, temperature and water tolerance versus time is depicted in Fig. 1. For paper impregnation on laboratory scale approximately 3–5 kg of liquid resin per experimental setting were consumed.

2.3 Resin characterization

Both MF and MUF impregnation resins were technologically characterized by measuring water tolerance, viscosity and curing time. Water tolerance in [%] was determined by adding water to the stirred resin at room temperature until precipitation resulted in a clear white color of the resin dispersion. Viscosity was determined as resin flow time in [s] using a flow cup viscosimeter according to DIN EN ISO 2431. Cure time in [min] was determined by heating the resin with a defined amount of reference catalyst in a test tube in boiling water until the resin was completely cured. Solids content was determined by drying and weighing the resins on a heated infrared balance until no more weight changes occurred.

2.4 Experimental design

To assess the effect of the type of impregnation resin (MF or MUF) on the technological parameters of impregnated

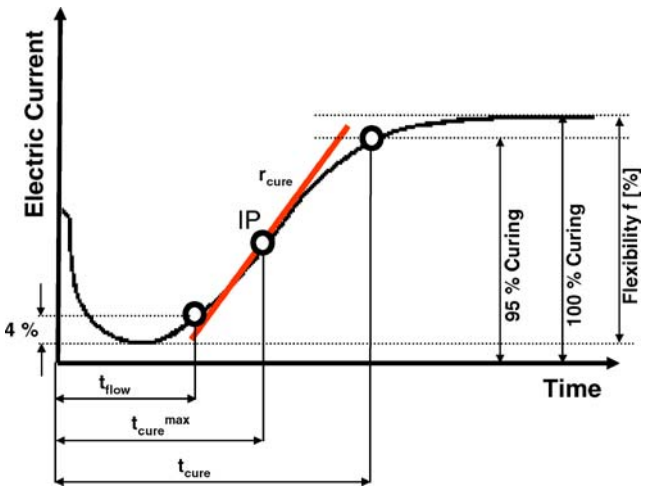

Fig. 1 Typical response curve of dynamic mechanical measurement using the Golombek-apparatus. IP, inflection point; t_{flow}, flow time; t_{cure}^{max}, time point of maximum curing rate; t_{cure}, time for 95% cross-linking of MF resin; r_{cure}, maximum curing rate

Abb. 1 Typisches Meßergebnis einer dynamisch-mechanischen Messung mit dem Golombek-Papiertester. IP, Wendepunkt; t_{flow}, Fließzeit; t_{cure}^{max}, Zeitpunkt, an dem die maximale Aushärtungsgeschwindigkeit erreicht wird; t_{cure}, Zeitpunkt, an dem ein Aushärtungsgrad von 95% des MF Harzes erreicht wird; r_{cure}, maximale Aushärtungsgeschwindigkeit

papers and coated boards, a full factorial experimental design was used (Petek et al. 2006). The parameters varied were resin type (MF, MUF), catalyst type (A, B, C or D), catalyst amount (5 levels: 0.1, 0.2, 0.3, 0.4 and 0.5% per weight resin solution) and pressing time (5 levels: 8, 10, 12, 16, and 20 seconds). Since all possible combinations were permutated a total of 100 different types of boards for each type of resin were produced. Each experimental setting was repeated twice for statistical reasons. Statistical evaluation of the experimental data set and generation of the response surface diagrams (Myers and Montgomery 2002) was performed using the computer program Design Expert 6.0.7 (Stat Ease Inc., Minneapolis, US).

2.5 Preparation of paper samples

Paper sheets of 30 cm × 30 cm were manually impregnated on a laboratory scale with either a MF or a MUF resin based impregnation solution of about 50% solids content containing different amounts of curing catalyst and additives. All four catalysts were supplied from BASF and were monobasic sulfonic acids containing different types and amounts of amine blocking agents. The number of acid groups present in the catalyst was determined prior to the impregnations by titration with sodium hydroxide solution. The catalyst amounts were normalized with respect to the catalytically active species. All impregnation solutions contained the same minimum amounts of additives essential for the processing (release agent $< 2\%$, antifoam agent $< 0.5\%$ and surfactant $< 1.5\%$).

In contrast to industrially manufactured papers which are impregnated in a two-step process, all laboratory papers prepared for this study were impregnated and coated in a single step using the same MF or MUF formulation for core impregnation and surface film formation. Impregnation was performed using a laboratory impregnation device (Munksjö Paper Decor GmbH & Co. KG, Aalen, Germany) with a 0.5 mm doctor blade and an electric propulsion control. The haul-off speed of the paper was 3 m min^{-1}, which was sufficiently slow to allow for complete core impregnation and to give smooth surface films without defects for all samples prepared. Impregnated paper sheets were dried in a drying oven for 90 s at 130 °C. Upon drying, paper weight and humidity was controlled. All papers were coated with 100 ± 5 g m^{-2} of resin to a respective final dry weight of ca. 170 g cm^{-2}. Final moisture content after drying was $6 \pm 0.5\%$ water per dry weight. Then the paper sheets were wrapped in thermoplastic foil to prevent moisture equilibration with the environment. Papers were kept in a conditioning chamber at room temperature (25 °C) and 50% relative humidity until further analysis and pressing. Papers were never kept longer than two days.

2.6 Testing of paper samples

2.6.1 Resin flow FR

Two sheets per experimental setting were used to determine the resin flow of the dry impregnated paper. Here, 6 rectangular samples of 96 mm × 60 mm were piled and the stack was pressed with a hydraulic press at 35 N cm^{-1} at 140 °C for 5 minutes. The weight of resin squeezed out of the stack was determined and is indicative of the liquefaction of the resin during the pressing step.

2.6.2 Dynamic mechanical measurements

Dynamic mechanical parameters of the impregnated papers were determined using the paper sheet tester developed by Golombek (Golombek 1991). This tester is widely used in the laminate industry and consists of an oil bath and a vertically adjustable sample holder coupled to a reversible rotary drive. The motor is connected to a galvanometer which allows continuous monitoring of the motor current required to move the paper sample (Kandelbauer and Teischinger 2008a).

Small sample sheets (96 mm × 60 mm) of impregnated paper were cut from the stored sheets and immersed in a hot silicone oil bath at 140 °C and the paper was cured. Oscillatory movements were performed at a frequency of 1 rpm and the consumed electrical current for performing the oscillations was recorded in dependence of time. While the impregnated paper was exposed to the hot silicone oil, resin curing took place and the stiffness of the paper increased due to cross-linking of MF resin. This increase was recorded during the test based on electrical current measurement. Figure 1 shows the time course of motor current versus time during a typical Golombek experiment and illustrates the definition of the various parameters accessible from the measurement.

The initial current value reflects the force required to move the not yet fully warmed, rather stiff paper sample. As the resin liquefies after being exposed to 140 °C the paper sample softens and its resistance against circular motion declines and correspondingly the energy consumption of the motor decreases. After passing through a minimum the current consumption increases since curing of the impregnation resin causes the paper stiffness to rise. At the inflection point (IP) the curing rate reaches its maximum and slows down again until the resin is completely cross-linked. The tests were finished when the impregnation resin was completely cured as indicated by no further increase in electric current. This typically was the case after approx. 5 minutes.

From the curve shown in Fig. 1 several rheological and thermal parameters were obtained such as the flow time t_{flow}, the curing rate r_{cure}, the time of maximum cure rate t_{cure}^{max},

the curing time t_{cure} and the flexibility f. Flow time, t_{flow}, is the time at 140 °C until the curing of the liquefied resin in the impregnated paper starts to significantly increase the current response. It is defined in relation to the minimum response as illustrated in Fig. 1. The curing rate, r_{cure}, is defined as the slope of the curve at the inflection point (IP, Fig. 1). Correspondingly, t_{cure}^{max}, represents the time where the curing process proceeds at the highest rate and is defined as the intercept with the x-axis at the inflection point. The curing time, t_{cure}, is defined as the time at which 95% of the cross-linking has occurred. Flexibility, f, is the percentage of cross-linking that can be reached with the liquefied resin. For its definition, also refer to Fig. 1. All parameters describe impregnated papers well and allow drawing conclusions on their technological performance.

Dynamic mechanical measurements were repeated twice for each sample. The average values of each response were used for response surface analysis (Myers and Montgomery 2002). In the current paper, the statistical analysis was focussed on f, t_{flow}, t_{cure} and r_{cure}. Since the remaining parameter t_{cure}^{max} yields no additional information it was considered redundant for the presented data material.

2.7 Preparation of boards

Ten paper sheets per experimental setting were used for the subsequent pressing experiments in order to generate two replicate samples for each differently coated board. All sheets were pressed together with particleboards of 7 mm thickness in a short-cycle laboratory press (Robert Bürkle GmbH, Freudenstadt, Germany) at 35 N cm^{-2} and 167 °C film contact temperature for various time periods.

2.8 Testing of boards

Standardized surface quality tests were used to characterize the technological performance of manufactured boards. Surface gloss was determined as the average from 10 measurements per board of the specular reflectance at an angle of 60°. Porosity was visually judged under a microscope after tinting an area of 25 cm^2 with soft pencil, subsequent rubbing out using a rubber and counting the remaining dark dots. The surface was classified according to an arbitrary scale from very good or "1" (no remaining stains of pencil) to very bad, or "5" (large areas of remaining pencil) in 0.5 unit intervals. The resistance of the boards towards chemical attack was similarly evaluated under the microscope by using the "acid value". The acid value was determined by treating a defined surface spot with concentrated hydrochloric acid for 15 min. Afterwards the surface was microscopically classified according to an arbitrary scale from very good or "1" (no attack of the surface by the acid) to very bad, or "5" (surface completely destroyed) in 0.5 unit intervals.

3 Results and discussion

3.1 MUF resin synthesis

In Fig. 2, the reaction-time profile of the MUF resin preparation is depicted. The synthesis on pilot scale took about two hours until the desired final water tolerance of 150% was achieved which was comparable to the range of water tolerance used with MF resins. The final properties of the MUF resin are similar to a commercial MF resin typical for paper impregnation and are summarized in Table 1.

3.2 Properties of MUF vs. MF impregnated decorative papers

A typical result from the dynamic mechanical measurements is shown in Fig. 3a,b. The results for the response surface

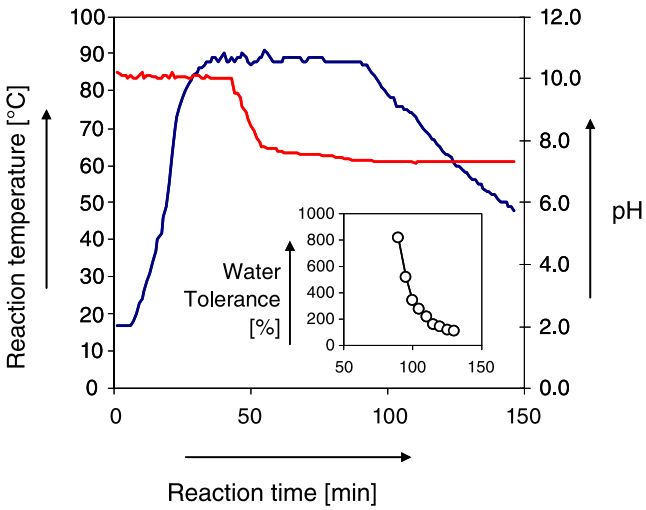

Fig. 2 Reaction profile for the preparation of the MUF impregnation resin showing the temperature (*full line*) and pH (*dotted line*) variations as a function of reaction time. The insert shows the dependence of water tolerance on the reaction time

Abb. 2 Reaktionsprofil für die Herstellung des MUF Imprägnierharzes, das den Temperaturverlauf (*durchgezogene Linie*) und den pH-Verlauf (*gestrichelte Linie*) in Abhängigkeit von der Reaktionszeit zeigt. Das Insert zeigt die Abhängigkeit der Wasserverträglichkeit des Harzes von der Reaktionszeit

Table 1 Selected properties of the impregnation resins used in this study

Tabelle 1 Ausgewählte Eigenschaften der in dieser Studie verwendeten Imprägnierharze

		MF	MUF
Water tolerance	[%]	150	150
Viscosity	[s]	27	28
Cure Time	[min]	3 : 30	4 : 21
Solids content	[%]	52	50
Urea content	[%]	0	30
(M + U)/F molar ratio		1:1.9	1:1.9

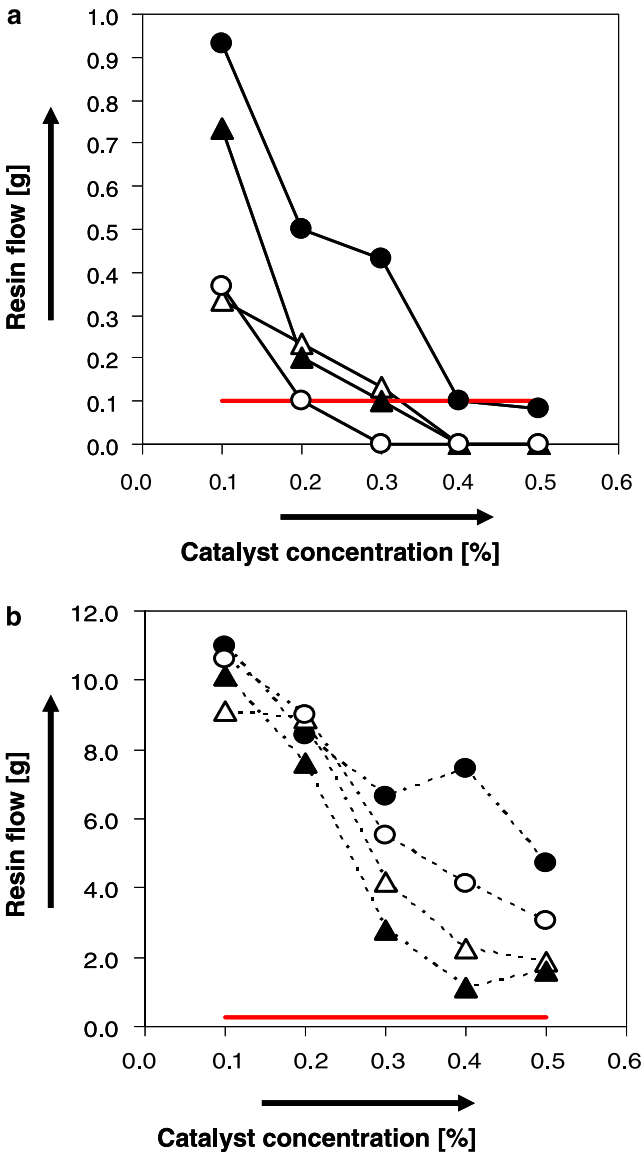

Fig. 3 Resin flow F in decorative papers impregnated with **a** MF and **b** MUF resin containing different amounts of the commercial curing catalysts A (●), B (○), C (▲) and D (△)
Abb. 3 Harzfluß F von Dekorpapieren nach Imprägnierung mit **a** MF- und **b** MUF-Harz bei verschiedenen Konzentrationen der vier kommerziellen Härtersysteme A (●), B (○), C (▲) und D (△)

analysis of the effects of amount and type of curing catalyst and the type of impregnation resin (MF or MUF) on the dynamic mechanical properties of impregnated decorative papers are summarized in Table 2. For the quantitative modeling, a 2-factor-interaction-(2FI)-model was found to describe best the experimental data set. The analysis of the effects showed that all factors tested in the experimental setup had a large influence on the dynamic mechanical properties of the impregnated papers. Moreover, all factors showed strong interaction effects meaning that for example when the type of resin was changed from MF to MUF the dependence of a response value such as flow on the catalyst type or amount would significantly change. All effects (including the interaction effects) were of comparable order of magnitude. The model accuracies for the different responses were $R^2 = 0.9486$ (resin flow), 0.9915 (flow time), 0.9258 (flexibility), 0.9872 (cure time) and 0.9948 (cure rate).

3.2.1 Resin flow

Resin flow is an important property of the impregnated paper which gives an indication of the degree of pre-condensation of the resin after the impregnation procedure. Resin flow must be sufficiently high for proper film formation to occur during the lamination in the hot press. The results for the flow measurements of impregnated papers containing varying amounts of different curing catalysts are shown in Fig. 3a (for MF) and Fig. 3b (for MUF). With increasing amounts of catalyst resin flow decreases for all different catalysts tested. Both MF and MUF resin impregnated papers behave similarly. The major difference is that by using MUF resin for impregnation, generally much higher values (approximately by a factor of 10) for resin flow were achieved. While MF papers containing higher amounts of catalyst sometimes showed already too low values for the resin flow, all MUF impregnated papers lay well above the lower limit of resin flow required for suitable processability of the papers. This means that by using MUF, production tolerances in terms of resin flow are easier to meet and a larger range of catalyst types can generally be used. A reason for this would be a much lower cross-linking degree of the resin since melamine reacts much more readily with formaldehyde than urea does (Pizzi 1994).

3.2.2 Curing behavior

The results for the curing behavior of MF and MUF impregnated papers are summarized in Fig. 4 (cure time) and Fig. 5 (cure rate).

With increasing amounts of curing catalyst, cure times decrease (Fig. 4) and cure rates increase (Fig. 5) with both MF and MUF resin. However, when MUF is used much slower curing processes are observed, MF obviously being much more reactive than the used MUF resin at 140 °C. Within the range of catalyst concentrations studied, MF resins seem to be better suitable for rapid board lamination. However, higher catalyst amounts could possibly provide faster curing rates with MUF.

3.2.3 Flow time

Flow time t_{flow} is an indicator for the length of the time period a resin still remains in a liquefied state during lamina-

Table 2 ANOVA results (partial sum of squares) for the response surface analysis of the responses flow, flow time, flexibility, cure time and curing rate of decorative papers impregnated with MF and MUF resins
Tabelle 2 ANOVA Ergebnisse (Partial Sum of Squares) für die Response-Surface-Analyse für die Zielgrößen „Fluß“, „Fließzeit“, „Flexibilität“, „Härtungszeit“ und „Härtungsgeschwindigkeit“ von Dekorpapieren, die mit MF- bzw. MUF-Harz imprägniert wurden

	F		t_{flow}		f		t_{cure}		r_{cure}	
	F-value	$P > F^a$	F-value	$P > F^a$	F-value	$P > F^a$	F-value	$P > F^a$	F-value	$P > F^a$
Model	735.79	< 0.0001	4648.42	< 0.0001	495.22	< 0.0001	3054.85	< 0.0001	7535.18	< 0.0001
[A]	1451.48	< 0.0001	9199.75	< 0.0001	2179.45	< 0.0001	9954.36	< 0.0001	38 220.93	< 0.0001
[B]	351.61	< 0.0001	1717.58	< 0.0001	573.57	< 0.0001	543.96	< 0.0001	2287.07	< 0.0001
[C]	11 698.33	< 0.0001	90 668.10	< 0.0001	3065.34	< 0.0001	68 527.00	< 0.0001	1.42×10^5	< 0.0001
[AB]	38.42	< 0.0001	25.64	< 0.0001	578.78	< 0.0001	1.98	0.1158	469.74	< 0.0001
[AC]	1551.63	< 0.0001	3645.14	< 0.0001	1333.38	< 0.0001	1598.77	< 0.0001	16 626.29	< 0.0001
[BC]	407.74	< 0.0001	646.87	< 0.0001	1095.62	< 0.0001	71.04	< 0.0001	2013.62	< 0.0001

F, resin flow; t_{flow}, flow time; f, flexibility; t_{cure}, cure time; r_{cure}, curing rate; [A], amount of curing catalyst in the impregnation resin mixture; [B], type of curing catalyst; [C], type of impregnation resin (MF or MUF)
[a] Values of "$P > F$" less than 0.05 (5%) indicate that model terms are significant

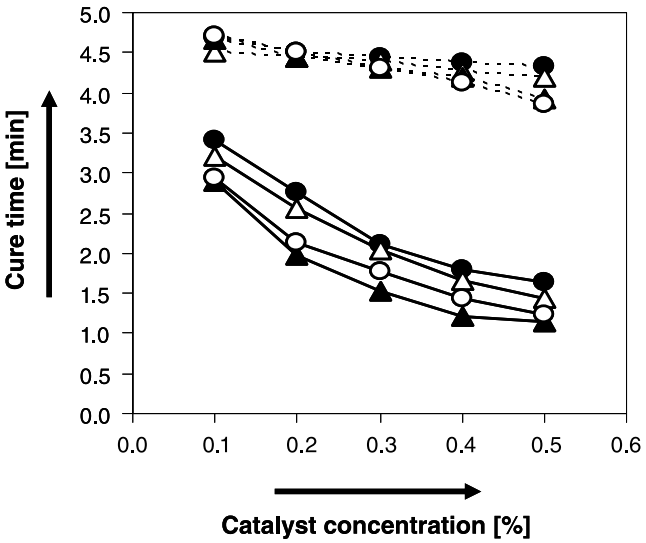

Fig. 4 Cure time t_{cure} of decorative papers impregnated with MF (*solid line*) and MUF (*dotted line*) resin containing different amounts of the commercial curing catalysts A (●), B (○), C (▲) and D (Δ) as measured with the Golombek dynamic mechanical analysis
Abb. 4 Härtungszeit t_{cure} von Dekorpapieren nach Imprägnierung mit MF-Harz (*durchgezogene Linie*) und MUF-Harz (*gestrichelte Linie*) bei verschiedenen Konzentrationen der vier kommerziellen Härtersysteme A (●), B (○), C (▲) und D (Δ), gemessen nach der dynamisch-mechanischen Methode nach Golombek

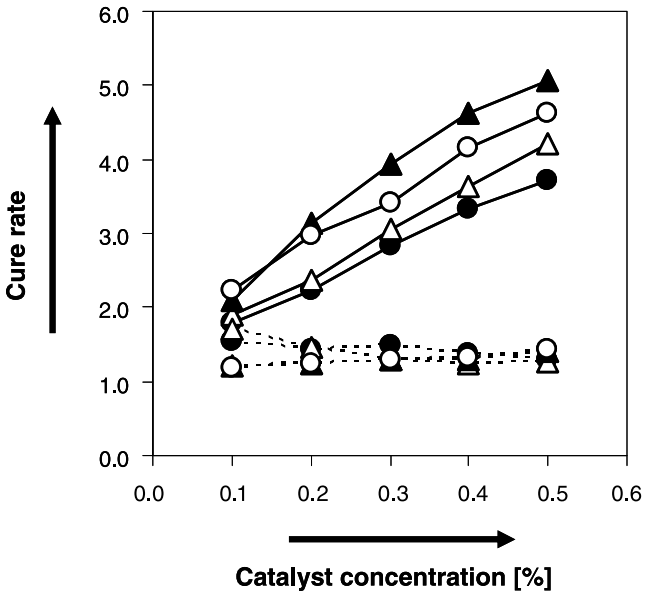

Fig. 5 Cure rate r_{cure} of decorative papers impregnated with MF (*solid line*) and MUF (*dotted line*) resin containing different amounts of the commercial curing catalysts A (●), B (○), C (▲) and D (Δ) as measured with the Golombek dynamic mechanical analysis
Abb. 5 Härtungsgeschwindigkeit r_{cure} von Dekorpapieren nach Imprägnierung mit MF-Harz (*durchgezogene Linie*) und MUF-Harz (*gestrichelte Linie*) bei verschiedenen Konzentrationen der vier kommerziellen Härtersysteme A (●), B (○), C (▲) und D (Δ), gemessen nach der dynamisch-mechanischen Methode nach Golombek

tion in the hot press. Papers with very low t_{flow} usually result in coated boards with low quality surfaces since no satisfactory resin films are formed. The results for the flow time are depicted in Fig. 6.

With both resins, an increase in catalyst concentration results in a decrease in t_{flow} for all catalysts used. As with F, t_{flow} of impregnated papers is much higher with MUF. From Fig. 6 it is also obvious that the useful working range of additive composition is significantly different for the two resin types. While with low catalyst amounts the film formation with MUF may not be finished in time during rapid pressing cycles, in the case of MF with high amounts of catalyst the film formation might already significantly be hampered due to much earlier resin solidification.

3.2.4 Flexibility

Flexibility is another important descriptor for impregnated papers and gives an indication of its cross-linking status. In highly flexible papers the degree of curing during lamination is high and hence a large portion of the resin remains yet uncured. On the other hand if f is too low, the remain-

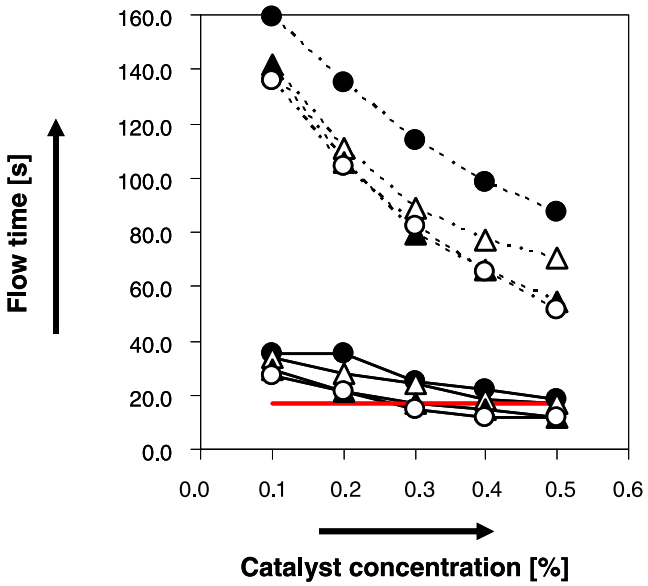

Fig. 6 Flow time t_{flow} of decorative papers impregnated with MF (*solid line*) and MUF (*dotted line*) resin containing different amounts of the commercial curing catalysts A (●), B (○), C (▲) and D (△) as measured with the Golombek dynamic mechanical analysis. The lower limit for the useful working range required for t_{flow} of industrial impregnated papers is indicated by the *solid line* at $t_{flow} = 20$ s

Abb. 6 Fließzeit t_{flow} von Dekorpapieren nach Imprägnierung mit MF-Harz (*durchgezogene Linie*) und MUF-Harz (*gestrichelte Linie*) bei verschiedenen Konzentrationen der vier kommerziellen Härtersysteme A (●), B (○), C (▲) und D (△), gemessen nach der dynamisch-mechanischen Methode nach Golombek. Die untere Grenze des vorteilhaften Arbeitsbereiches für die Fließzeit t_{flow} von industriell imprägnierten Dekorpapieren ist durch die *durchgezogene Linie* bei t_{flow} von 20 s angegeben

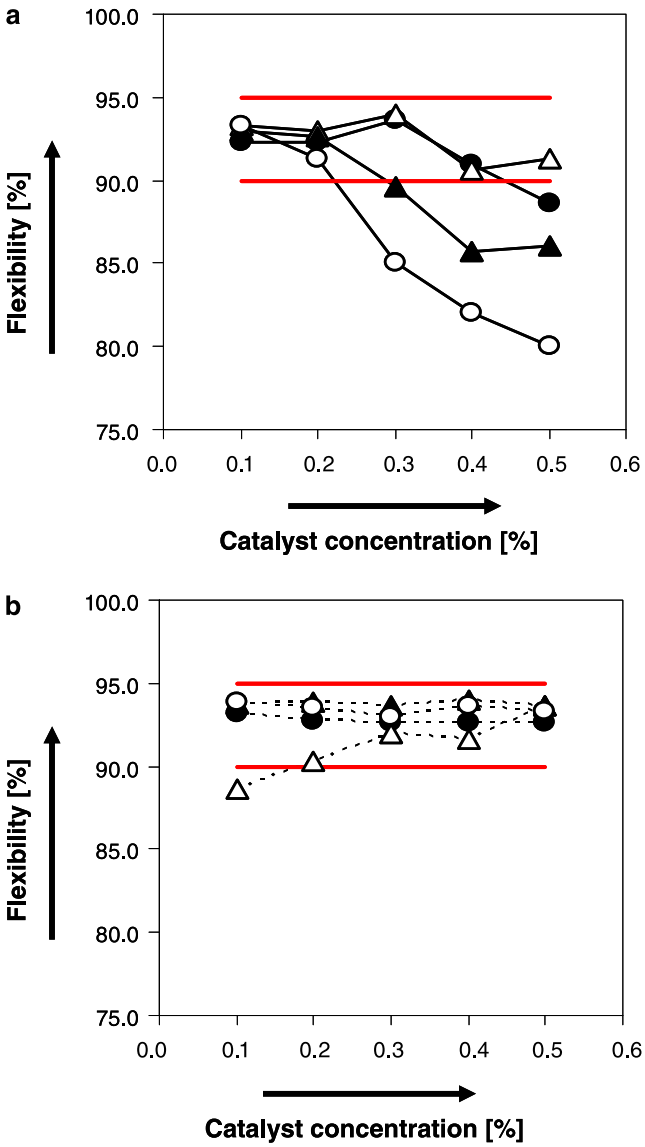

Fig. 7 Flexibility f of decorative papers impregnated with MF (*solid line*, **a**) and MUF (*dotted line*, **b**) resin containing different amounts of the commercial curing catalysts A (●), B (○), C (▲) and D (△). The upper and lower limits for the useful working range required for f of industrial impregnated papers is indicated by the *solid lines* as $95 < f < 90\%$

Abb. 7 Flexibilität f von Dekorpapieren nach Imprägnierung mit MF-Harz (*durchgezogene Linie*, **a**) und MUF-Harz (*gestrichelte Linie*, **b**) bei verschiedenen Konzentrationen der vier kommerziellen Härtersysteme A (●), B (○), C (▲) und D (△), gemessen nach der dynamisch-mechanischen Methode nach Golombek. Die obere Grenze des vorteilhaften Arbeitsbereiches für die Flexibilität f von industriell imprägnierten Dekorpapieren ist durch den Bereich zwischen den beiden *durchgezogenen Linien* (mit $95 < f < 90\%$) angegeben

ing activity may not be sufficient for proper lamination and the surface coating may not be considered as self-gluing anymore. Values of $f \ll 80$ typically result in a deficient surface finish prone to delamination; values above 90 are desirable for excellent mechanical performance. The results for the flexibility are summarized in Fig. 7a (MF) and Fig. 7b (MUF).

On average, the flexibility of MUF impregnated papers is higher and within a narrower range for all the different curing catalysts tested. With high catalyst concentrations MF films tend to be significantly less flexible. With one especially aggressive catalyst even values close to 80 were obtained that imply an especially high risk of delamination in the finished boards (Kandelbauer and Teischinger 2008b). In contrast, MUF papers were found to be within the optimum operation range practically in all cases and the nature of catalyst had no strongly pronounced effect on the flexibility.

Based on the properties of MUF impregnated decorative papers the performance of MUF for laminated board would be expected to be comparable to MF. Considering the formation of smooth surface films, even slightly better results would be expected with MUF whereas with respect to production speed MF should allow for higher throughputs in short-cycle presses due to the higher reactivity of the studied systems.

3.3 Properties of MUF vs. MF coated particleboards

The results for the response surface analysis of the effects of amount and type of curing catalyst, the type of impregnation resin (MF or MUF) and the pressing time during laminate formation on some technological properties of particleboards coated with impregnated decorative papers are summarized in Table 3. For the quantitative modeling of the target values studied for the boards (acid value, porosity and gloss), a two-factor interaction (2FI) model including all single-factor effects ([A], [B], [C] and [D]) as well as all interaction effects ([AB], [AC], [AD], [BC], [BD] and [CD]) (see Table 3) fitted best the measured data and the response surfaces were calculated as the linear combinations given in (1)–(3).

$$\begin{aligned}\text{Acid value} = &-1.83-4.16[\text{A}]-1.62[\text{B}_1]-1.72[\text{B}_2]\\ &+1.40[\text{B}_3]+0.55[\text{C}]+3.23[\text{D}]\\ &-2.03[\text{AB}_1]-2.25[\text{AB}_2]+1.79[\text{AB}_3]\\ &+0.50[\text{AC}]+4.13[\text{AD}]+0.034[\text{B}_1\text{C}]\\ &+0.13[\text{B}_2\text{C}]-0.074[\text{B}_3\text{C}]-0.11[\text{B}_1\text{D}]\\ &-0.18[\text{B}_2\text{D}]+0.10[\text{B}_3\text{D}]-0.17[\text{CD}] \qquad (1)\end{aligned}$$

$$\begin{aligned}\text{Porosity} = &\ 0.94-3.01[\text{A}]-4.84[\text{B}_1]-0.86[\text{B}_2]\\ &+1.76[\text{B}_3]+0.016[\text{C}]+1.31[\text{D}]\\ &-6.29[\text{AB}_1]-1.45[\text{AB}_2]+2.46[\text{AB}_3]\\ &-0.24[\text{AC}]+1.75[\text{AD}]+0.077[\text{B}_1\text{C}]\\ &+0.25[\text{B}_2\text{C}]-0.27[\text{B}_3\text{C}]-0.041[\text{B}_1\text{D}]\\ &+4.658\times10^{-4}[\text{B}_2\text{D}]-1.457\times10^{-3}[\text{B}_3\text{D}]\\ &-0.015[\text{CD}] \qquad (2)\end{aligned}$$

$$\begin{aligned}\text{Gloss} = &\ 147.23+125.52[\text{A}]+3.31[\text{B}_1]-15.88[\text{B}_2]\\ &+10.01[\text{B}_3]-25.57[\text{C}]-19.70[\text{D}]\\ &+9.67[\text{AB}_1]-17.50[\text{AB}_2]+8.63[\text{AB}_3]\\ &-15.34[\text{AC}]-23.99[\text{AD}]-1.96[\text{B}_1\text{C}]\\ &+1.31[\text{B}_2\text{C}]+0.18[\text{B}_3\text{C}]+1.34[\text{B}_1\text{D}]\\ &-0.32[\text{B}_2\text{D}]-0.48[\text{B}_3\text{D}]-0.88[\text{CD}] \qquad (3)\end{aligned}$$

The analysis of the effects showed that all single factors tested in the experimental setup had a large influence on the properties of the boards. Moreover, most factors showed strong interaction effects meaning that for example when the type of resin was changed from MF to MUF the dependence of a response value such as gloss on the pressing time would significantly change. All effects (including the interaction effects) were of comparable order of magnitude. The model accuracies for acid value and porosity were $R^2 = 0.6535$ (acid value), 0.5733 (porosity) and thus were significantly worse than those for the impregnated paper properties. The reason for this is that in these cases no continuous scale of measurement values was available. In contrast, the correlation coefficient for surface gloss was again much better ($R^2 = 0.9748$). In any case, both the model and the effects were statistically significant (Table 3) whereas the lack of fit was not significant. This means that although the robustness and predictive power of the models for acid value and porosity are not excellent they still reflect the actual trends.

3.3.1 Acid value

The acid value AV of a coated particle board gives an indication of the chemical resistance of the surface. Low values for AV (AV < 3) mean that the surface is hardly attacked by hydrochloric acid and the film quality is good. Figure 8a–d shows contour line plots from the response surface analysis for the acid value of particle boards coated with MF (Fig. 8a and b) and MUF (Fig. 8c and d).

In response surface analysis theoretical values for a certain technological target property (=response) are calculated using a regression model which is based on the experimental factors that have a statistically significant influence on this response. The corresponding contour line plots show

Table 3 ANOVA results (partial sum of squares) for the response surface analysis of the responses acid value, porosity and gloss for particleboards coated with MF and MUF resin impregnated decorative paper
Tabelle 3 ANOVA Ergebnisse (Partial Sum of Squares) für die Response-Surface-Analyse für die Zielgrößen „Säurewert", „Porosität" und „Glanz" für Spanplatten, die mit MF bzw. MUF Harz imprägnierten Papieren beschichtet wurden

	AV		*P*		*G*	
	F-value	$P > F^a$	*F*-value	$P > F^a$	*F*-value	$P > F^a$
Model	74.83	< 0.0001	53.32	< 0.0001	1535.62	< 0.0001
[A]	472.99	< 0.0001	61.54	< 0.0001	1445.95	< 0.0001
[B]	77.02	< 0.0001	220.30	< 0.0001	94.30	< 0.0001
[C]	116.09	< 0.0001	166.56	< 0.0001	4697.68	< 0.0001
[D]	397.54	< 0.0001	36.05	< 0.0001	16.74	< 0.0001
[AB]	45.86	< 0.0001	44.28	< 0.0001	3.80	0.0100
[AC]	5.55	0.0187	0.34	0.5606	15.48	< 0.0001
[AD]	158.59	< 0.0001	7.29	0.0071	15.60	< 0.0001
[BC]	28.33	< 0.0001	31.44	< 0.0001	14.10	< 0.0001
[BD]	25.95	< 0.0001	0.23	0.8742	1.90	0.1284
[CD]	85.95	< 0.0001	0.18	0.6679	6.94	0.0086

AV, acid value; *P*, porosity; *G*, gloss; [A], amount of curing catalyst in the impregnation resin mixture; [B], type of curing catalyst; [C], type of impregnation resin (MF or MUF) ; [D], pressing time
[a] Values of "$P > F$" less than 0.05 (5%) indicate that model terms are significant

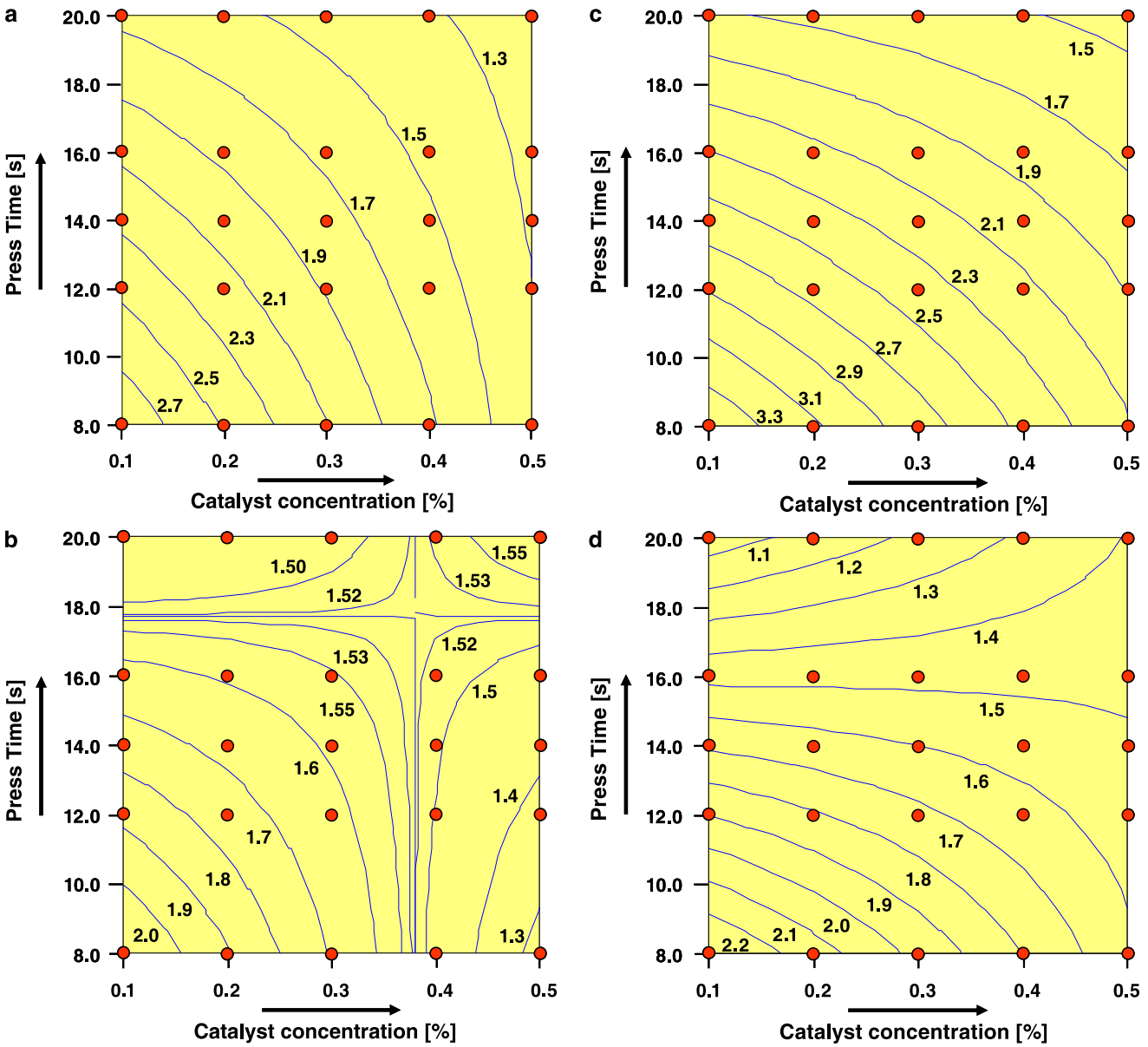

Fig. 8 Contour line plot of the response surface analysis for the acid value of particle boards laminated with MF (**a**, **b**) and MUF (**c**, **d**) resin impregnated decorative papers containing different amounts of commercial curing catalysts A (**a**, **c**) and B (**b**, **d**) at varying press times. *Dots* in the contour plot indicate actual experimental settings

Abb. 8 Konturlinien-Plot der Response Surface Analyse für den Säurewert von Spanplatten, die mit MF- (**a**, **b**) and MUF- (**c**, **d**) Harz imprägnierten Dekorpapieren mit verschiedenen Konzentrationen der beiden kommerziellen Härtersysteme A (**a**, **c**) und B (**b**, **d**) bei verschiedenen Presszeiten beschichtet wurden. Die *Punkte* im Konturlinien-Plot bezeichnen tatsächlich durchgeführte Experimente

two-dimensional projections along the *z*-axis of the three-dimensional response surfaces that were calculated from the 2FI-models (Eqs. 1 to 3) for different combinations of catalyst concentration (*x*-axis) and press time (*y*-axis) within the experimental range of factor settings. None of the contour lines in Fig. 8a–d are straight lines. They are all curved and hence the response surfaces for the acid values have a curved shape in the three-dimensional space. This reflects the non-linear interaction of the numerical factors "press time" and "catalyst concentration" which is typical for 2FI-models. It is important to note that such interactions are impossible to detect with experiments where only one factor at a time is varied while all the others are kept constant (Petek et al. 2006). Dots in the figures represent combinations of pressing times and catalyst concentration which were actually used in the experiments.

Each contour line represents combinations of press time and catalyst concentrations that lead to equal values in the target response. For example all three combinations: 20 s/0.25%; 17 s/0.35% and 8 s/0.46% of press time/cata-

lyst would lead to boards having an acid value of 1.5 as shown in Fig. 8a. Contour lines to the left of the 1.5-line (combinations of shorter press dwelling times with lower catalyst percentages) would represent parameter settings leading to worse board quality whereas all parameter combinations to the right of the 1.5-line would yield boards with improved properties.

The response surface profile with both resin types depended on the type of curing catalyst mixed with the resin. With catalyst A, in the case of MF (Fig. 8a), best results were obtained when both high levels of catalyst were used in combination with long pressing times. This indicates that board quality improves when the conditions are favorable for sufficient curing of the surface. A similar result was obtained for the same catalyst when used in MUF (Fig. 8c). Although board quality was slightly worse in this case unusable boards were only obtained with very low catalyst concentrations in combination with very short pressing times. With catalyst B, in the case of MF (Fig. 8b) generally lower values for AV were obtained. However, a plateau was observed when the combinations high catalyst level/long pressing times were employed. This indicates that not in any case an improvement in surface quality may be achieved by simply improving resin cure. With very harsh curing conditions even deterioration of surface quality can be observed meaning that a too high extent of resin cure may lead to surface defects impeding chemical resistance and other surface properties (Kandelbauer et al. 2007). The shapes of the response surfaces shown in Fig. 8a and 8c for catalyst B resemble the lower left quadrant of Fig. 8b whereas the shape depicted in Fig. 8d fits the upper and lower left quadrants. With MUF and catalyst B (Fig. 8d), the best boards were obtained with relatively low catalyst amounts but rather long pressing times.

In summary, with both resin types coated boards of very good chemical resistance can be prepared by suitable choice of the resin formulation (catalyst content) and the laminating conditions (pressing times).

3.3.2 Porosity

Porosity P of a coated particle board gives an indication of the affinity of the surface toward dirt particles. P-Values for laboratory boards of $P < 3$ mean that the surface film quality is sufficiently well and corresponding industrially manufactured boards will display excellent cleanability. Figure 9 shows a contour line plot from the response surface analysis for P of particle boards coated with MUF containing various catalyst levels and laminated with different pressing times.

With high pressing times, very good values for P are obtained. A combination of high pressing times with large amounts of catalyst seems not to be favorable in this case. However, when choosing a different catalyst type better results are obtained with both factors being set to higher values

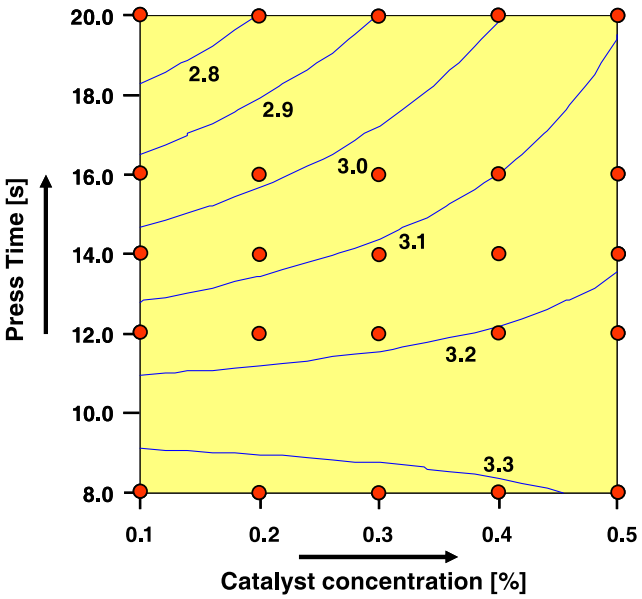

Fig. 9 Contour line plot of the response surface analysis for the porosity of particle boards laminated with MUF resin impregnated decorative papers containing different amounts of curing catalyst at varying press times. *Dots* in the contour plot indicate actual experimental settings
Abb. 9 Konturlinien-Plot der Response Surface Analyse für die Porosität von Spanplatten, die mit MUF-Harz imprägnierten Dekorpapieren mit verschiedenen Härterkonzentrationen bei verschiedenen Presszeiten beschichtet wurden. Die *Punkte* im Konturlinien-Plot bezeichnen tatsächlich durchgeführte Experimente

(data not shown). The response surface diagrams for MF look similar to those obtained for the corresponding MUF coated boards; however, the values for P are slightly better in most cases. The trends observed with P parallel very much the trends found for AV indicating that better curing of the paper resin generally improves the board quality as long as excess cross-linking is avoided.

3.3.3 Gloss

The shapes of the response surfaces from gloss analysis of MF and MUF coated particleboards are shown in Fig. 10a (MF) and Fig. 10b (MUF). The contour line plots are representative for all different catalysts tested in this study. The curvature of the contour lines is not very pronounced illustrating that the interaction between pressing time and catalyst concentration is less pronounced as with the other target responses.

Gloss generally increased when higher amounts of curing catalyst were employed. The dependence on pressing time was much less pronounced, although longer dwelling times resulted in slightly higher values for gloss. The major difference between the two resin systems is that with MUF only matt surfaces were obtainable. Although for all laminations glossy press plates were used, high gloss surfaces

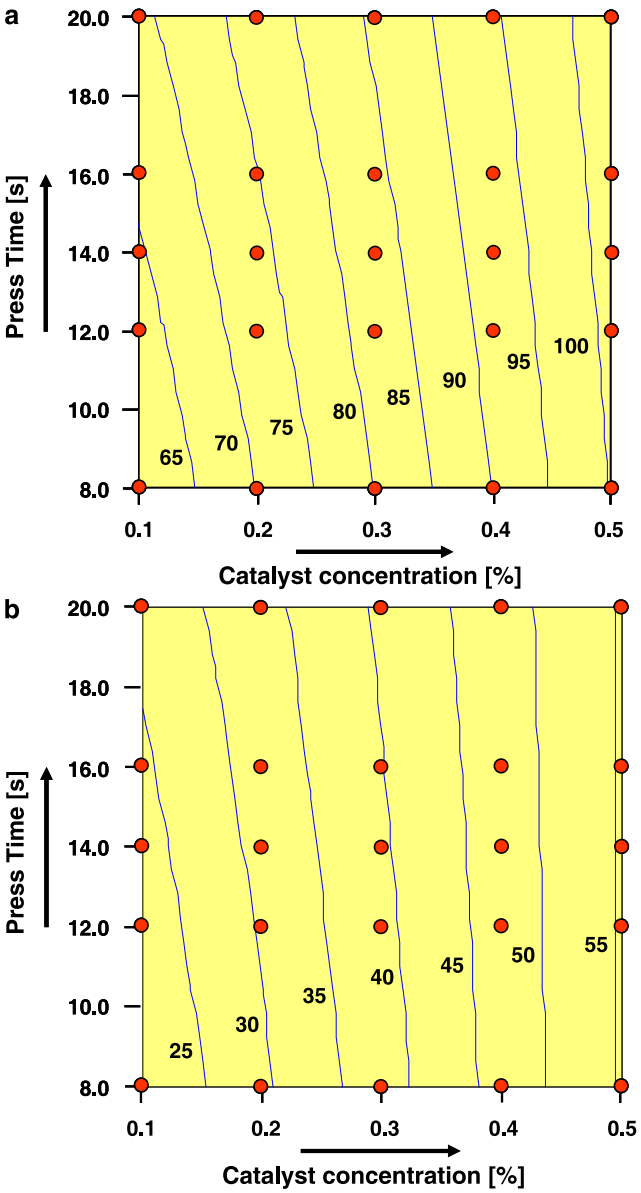

Fig. 10 Contour line plot of the response surface analysis for the gloss of particle boards laminated with **a** MF and **b** MUF resin impregnated decorative papers containing different amounts of curing catalyst and laminated at varying press times. *Dots* in the contour plot indicate actual experimental settings

Abb. 10 Konturlinien-Plot der Response Surface Analyse für den Glanz von Spanplatten, die mit **a** MF-Harz und **b** MUF-Harz imprägnierten Dekorpapieren mit verschiedenen Härterkonzentrationen bei verschiedenen Presszeiten beschichtet wurden. Die *Punkte* im Konturlinien-Plot bezeichnen tatsächlich durchgeführte Experimente

($80 > G > 100$) were only generated with well cured MF films.

4 Conclusion

Based on the findings in the present study, MUF may present a promising alternative to MF in the surface finishing of MDF and particleboards with impregnated decorative papers. The properties of liquid MUF were within the same range as a typical MF and the impregnation of papers on a laboratory scale was performed without any problems according to the standard procedure used with MF. Processability of MUF impregnated papers was sufficiently good and in some properties even exceeded the requirements expected from papers such as for flexibility or flow time. However, the curing of MUF papers was significantly slower than that of MF papers. This was reflected also by the final board properties measured. However, it was always possible to find combinations of the experimental factors catalyst amount and pressing time that allowed for sufficient chemical resistance and cleanability of MUF coated boards except for surface gloss. Highly glossy surfaces were only obtained with MF impregnated papers. Then again, in the present study only a limited range of catalyst concentrations and pressing times were studied. It seems plausible that an optimization of the curing conditions required for MUF may lead to even better results. More reactive MUF resins might be designed that fit better the requirements of fast laminating of boards in short-cycle presses. In addition, MUF films need to be tested for other properties as well, such as scratch resistance, abrasion resistance or light stability which are interesting for other applications such as for example in floorings.

In short, within the range of experimental conditions studied the overall technological performance of MUF coated boards was found to be comparable to that of the corresponding pure MF based laminates. In some cases MF may actually be substituted by MUF for the manufacturing of decorative surfaces thereby reducing significantly the production cost.

Acknowledgement The authors would like to thank Muhammad Houberdon (ENSTIB), Horst Schreiner (K WOOD) and especially Iris Taudes (K WOOD) for their great affords in numerous preparative experiments that lead to the final procedure of the MUF resin described above. The authors would also like to thank the representatives of Impress Décor Austria GmbH for their cooperation in performing the technological testing and permitting the publication of the presented data. This work was funded by the Austrian Research Promotion Agency FFG within the COMET program line.

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