

CURING CHARACTERIZATION ON LAMINATES BY DIELECTRIC ANALYSIS AND CORRELATION WITH SURFACE PROPERTIES

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Abstract

Dielectric analysis (DEA), also referred to as impedance spectroscopy, is a well-known method for characterizing the polymerization reactions of non-aqueous, radical or polyadditive systems. Nowadays, this method represents also an interesting way for the cure monitoring of aminoplastic resins. The adhesive's degree of curing is a key factor for the quality of laminates.

In the present study, the applicability of DEA on melamine-formaldehyde (MF) impregnated papers has been tested. Curing of industrial MF resin laminated panels were successfully determined by DEA via ion viscosity monitoring. The changes in the dielectric properties were detected directly during the hot pressing process by an increase of the ion viscosity. The starting minimum ion viscosity value is higher if the sample is pre-dried and pre-cured. DEA data was compared with enthalpy values from DSC and storage moduli from DMA.

Interestingly, if the pressing time is as usually very short, a major part of the cross-linking occurs mainly after the actual hot pressing. The degree of curing of the final product can be determined in a second measurement. The obtained data correlate well with the laminate's surface properties.

Key words: *curing characterization; dielectric analysis; laminate; melamine-formaldehyde resin; surface quality.*

INTRODUCTION

The quality of lamination and particularly the surface properties of laminated wood panels (as stability, gloss or hardness) are not only defined by the type of adhesive used, but also by the resins' degree of curing. To define an optimized cross-linking degree it is necessary to optimize the hot pressing which is related with intensive time and material investment. Basically, for any change of the resin composition, pressing parameters have to be optimized. In the engineered wood industry, the degree of curing is only defined by typical mechanical labor-intensive and time-consuming quality tests as bending, traction or scratching. An in-line control of these processing steps would be desirable. Spectroscopic methods, ultrasonic measuring system and dielectric analysis (DEA) could provide possibility for the in-line measurement of cross-linking reactions. However, during the hot press process of resin based wood composites is DEA more applicable because of its measurability over a large area. In the ideal case, the implementation of dielectric analysis would allow a prediction of selected properties based on signal changes during the production.

The materials' dielectric properties are measured by DEA as a function of time, frequency and temperature. The method is based on the fact, that an immobilization of molecular groups during polymerization causes a decrease in the dielectric conductivity. The sample is usually in contact with an interdigitated electrode sensor. The signals are detected by applying an alternating electrical field

on the sample. This methodology has been introduced in the wood glue industry during the last decade and first DEA studies on polycondensating resins were reported (Wang and Winistorfer 2003; Sernek and Kariz 2009; Jost and Sernek 2009; Pretschuh et al. 2012a, Pretschuh et al. 2012b, Pretschuh et al. 2013). Our own DEA experiences on the curing detection of aminoplastic resins showed us influences caused by drying processes and by the addition of ionic curing agents. Furthermore we detected the possibility of analyzing post-curing reactions by DEA.

Within the scope of our research project, DEA was applied on powder coatings systems as well as on aqueous aminoplastic resin systems for wood panels, particle boards and for impregnated papers. Correlations of DEA with ex-situ methods (DSC, rheological methods and mechanical tests) were performed.

OBJECTIVE

The main objective of this presented research part was to test the applicability of DEA as a cure monitoring system for aminoplastic resins during an industrial hot press laminating process. The study contains DEA analysis on pre-dried melamine-formaldehyde (MF) impregnated laminates at a constant heating rate and at varied isothermal pressing temperatures. Correlations of DEA with curing enthalpy values (DSC) were carried out. Therefore, the occurring processes during the hot pressing, drying and cross-linking, were splitted into two functions.

MATERIAL, METHOD, EQUIPMENT

MF impregnated papers were prepared in laboratory scale by inserting the paper in aqueous 50% MF Kauramin® solution (without curing agent) and pre-drying at 130°C. Typical industrial laminates, based on MF with curing agent, were provided from FunderMax.

Dielectric Analysis (DEA)

DEA was performed in multi-frequency mode at 10 Hz, 100 Hz, 1 kHz and 10 kHz or in single-frequency mode at 1 kHz or 10 kHz on a NETZSCH DEA cure monitor Epsilon 230/1, using an interdigitated electrode sensor (NETZSCH IDEX) with an electrode distance of 115µm. MF impregnated papers were analyzed in laboratory scale between wood veneer joints. The sensor was mounted on the paper sample and the alignment was transferred into a laboratory hot press and fixed at 10 Ncm⁻². The laminates were further analyzed on a 16 mm particle board, both at the laboratory press (at 150 Ncm⁻²) and on a pilot scale press (at 294 Ncm⁻²). For the pilot scale experiments the sensor was fixed on the impregnated laminate at the top of a sandwich construction (stabilizing layer, particle board, underlay paper and decorative laminate).

DEA at constant heating rates were performed by transferring the laboratory measuring setup (laminate between wood veneer joints) into an DEA NETZSCH oven system. For further correlations the oven of a TA instruments DMA Q800 was used. In this case, a mini-IDEX sensor was placed between the laminate and the veneer and the setup was fixed in a 3-point bending clamp.

Ion conductivity, permittivity, loss factor, dissipation factor and the ion viscosity are values which can be displayed by DEA cure monitor from NETZSCH. In our research we interpret the logarithmic ion viscosity development. The ion viscosity is a multiplicative inverse of the ion conductivity, according to equation 1.

$$IonVisc = \frac{1}{\sigma} = \frac{1}{\epsilon'' \epsilon_0 \omega} = \frac{RA}{d} \quad [\Omega m] \quad (1)$$

where:

σ is the ion conductivity, calculated from the measured resistance (R). The ion conductivity is defined as a product from permittivity and angular-frequency.

ϵ'' is the imaginary part of relative permittivity (loss factor) and ϵ_0 the permittivity in the vacuum.

ω is the angular frequency ($2 \pi f$).

R is the equivalent AC parallel resistance (impedance).

A is the electrode area and d the distance between electrodes.

Curing Enthalpy

Enthalpy values from exothermic curing peaks were determined by DSC measurements on MF impregnated papers and laminates. The experiments were performed in hermetic pans using a TA Instruments DSC Q20. The DSC conversion was calculated as integral function from the exothermic curing peak.

Laminate Surface

Standardized quality tests were used to characterize the laminate surface. The gloss of the obtained surface was measured using a specular reflectance measurement system at an incident angle of 60°. The acid stability value was classified on a scale from 1 to 5 after treating the surface with concentrated hydrochloric acid for 15 min (“5” for no damage on the surface and “1” for surface completely destroyed).

RESULTS AND DISCUSSION

Curing Detection by DEA

A typical curve progression showing an increase of the logarithmic ion viscosity during the cross-linking of a MF adhesive is shown in Fig. 1. The final isothermal temperature between the 2mm thick wood veneers is reached in the hot press after 2 min. In this time interval the ion viscosity, as an inverse to ion conductivity, decreases due to temperature increase, melting and diffusion effects. During the following isothermal phase the logarithmic ion viscosity highly increases due to the cross-linking reactions. DEA analysis during a constant heating ramp (Fig. 2) clearly illustrates the effect of the temperature increase.

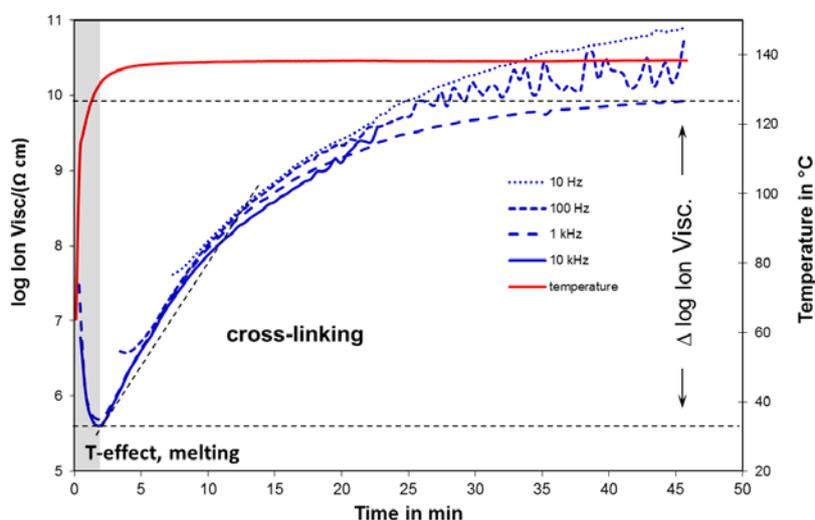


Fig. 1.
Typical DEA signals of an aqueous MF resin during isothermal cross-linking

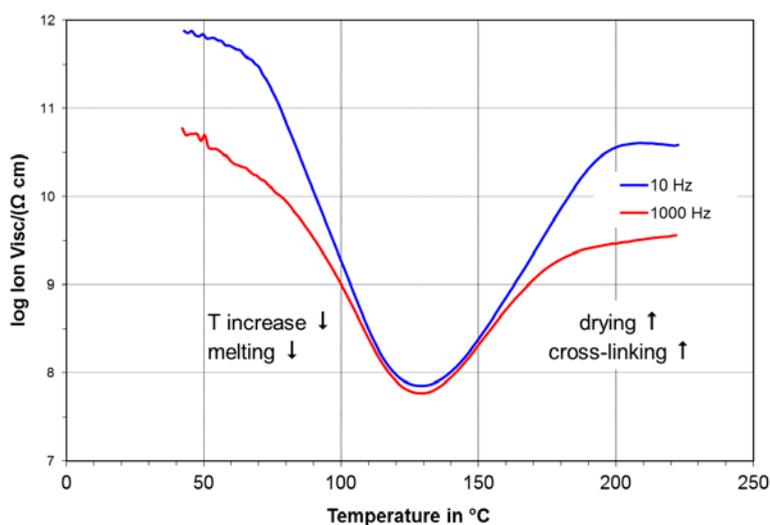


Fig. 2.
DEA measurement on a MF laminate during a constant heating ramp

Fig. 3 shows DEA results of two differently pre-dried MF impregnated papers during hot pressing. Longer drying results in lower water content and a higher pre-curing degree, so the logarithmic ion viscosity's starting values are higher.

Fig. 4 represents the temperature-dependence of the ion viscosity increase of MF laminates. As expected, the curing rate is consistently increasing with higher pressing temperatures. Typical pressing times in real production processes are shorter than 1 min. However, our DEA measurements show only a slightly increase of the ion viscosity during this short pressing time at all. So the question remains whether the curing takes place during this short time or not? We suppose that cross-linking reactions are only initiated and the major part of cross-linking reactions takes place outside the press, during the cooling episode.

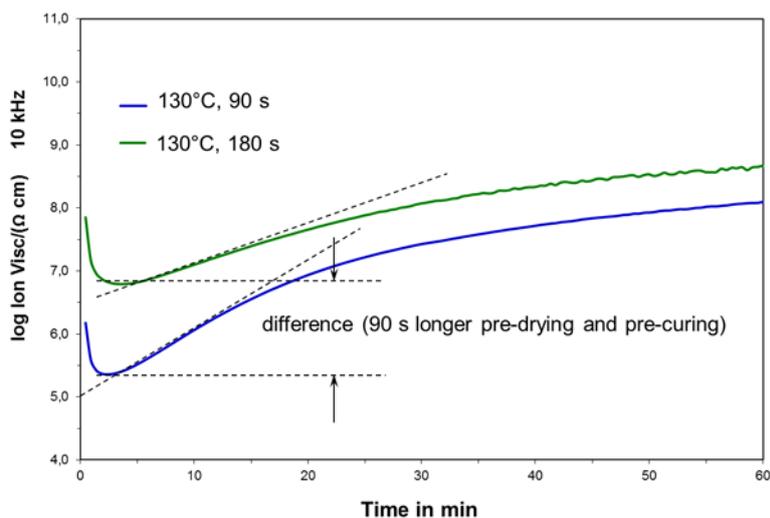


Fig. 3.

DEA signals of differently pre-dried MF impregnated papers during pressing at 100°C (between wood veneer joints)

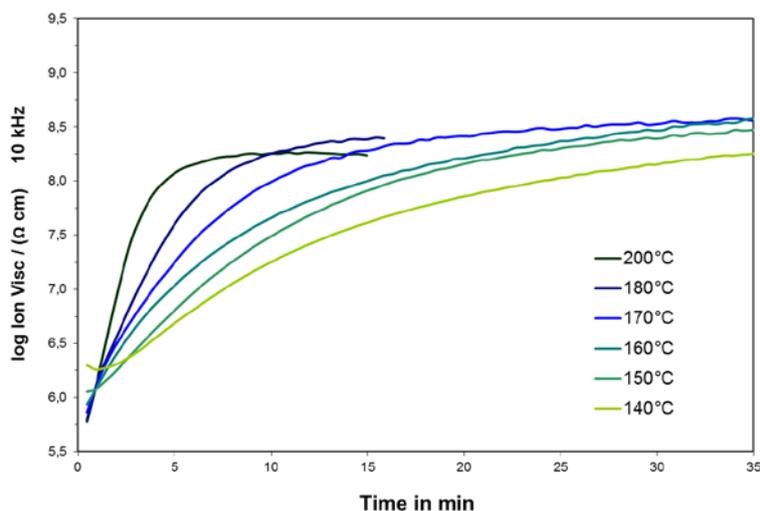


Fig. 4.

Temperature dependence of the cross-linking of industrial laminates (laboratory press) measured by DEA

Correlation with Enthalpy (DSC)

For an evaluation of the DEA data, we performed DEA measurements on a MF laminate at a constant heating rate for a comparison with curing enthalpy values from analogous DSC experiments at the same heating rate. This DEA measurements were carried out in a DMA 3-point bending setup. Fig. 5 represents the obtained DEA data. By using Origin data analysis software, we split the ion

viscosity data in a decreasing function for the temperature depending softening effects (Boltzmann function) and in an increasing function for the cross-linking part (Gompertz function). This simulated DEA data received from the 3-point bending test, as presented in Fig. 5, was compared with the conversion curve from DSC results (Fig. 6). DSC conversion and the cross-linking DEA simulation curve are starting at the same temperature, but at higher curing degrees DEA seems to be a more sensitive method. This correlation indicates that the ion viscosity increase could be a suitable value for the characterization of the MF resin curing.

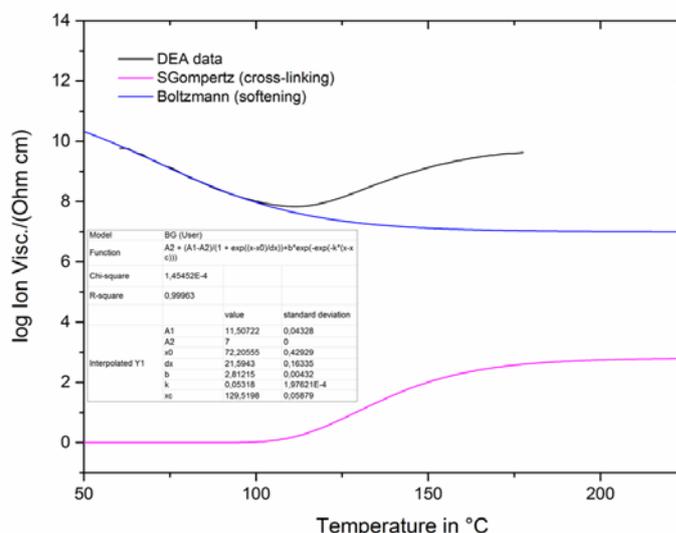


Fig. 5.

DEA data at 1 kHz from a 3-point bending setup at constant heating rate of 3 K min⁻¹, with a fit of the ion viscosity into two sigmoide functions for the separation of the softening and the cross-linking part

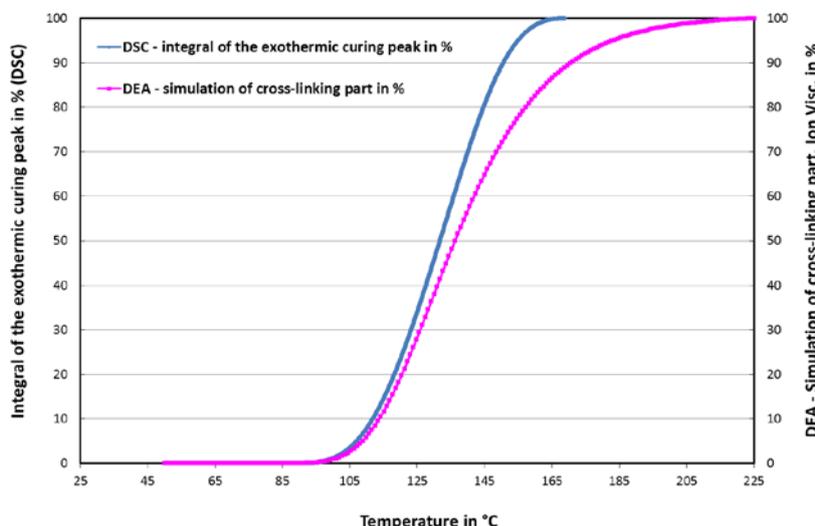


Fig. 6.

Simulated DEA cross-linking curve (Figure 5) correlated with exothermic curing conversion from DSC measurement

Curing Degree from Short-time Pressed Laminated Samples by DEA

To enable the curing detection of short-time pressed laminates, we analyzed the samples in a subsequent pressing run by DEA. The dashed lines in Fig. 7 show the logarithmic ion viscosity developments during these second pressing runs of differently short-time pressed samples. As

comparison, the continuous line represents the ion viscosity during a long one-time pressing. The laminated samples with higher (pre)-curing degrees exhibit higher ion viscosity starting values. For example, an increase of the logarithmic ion viscosity from 6 to 7.5 is related to a curing at 180°C for 30s. We suppose that this increase of the ion viscosity starting value is directly correlated with the extent of cross-linking.

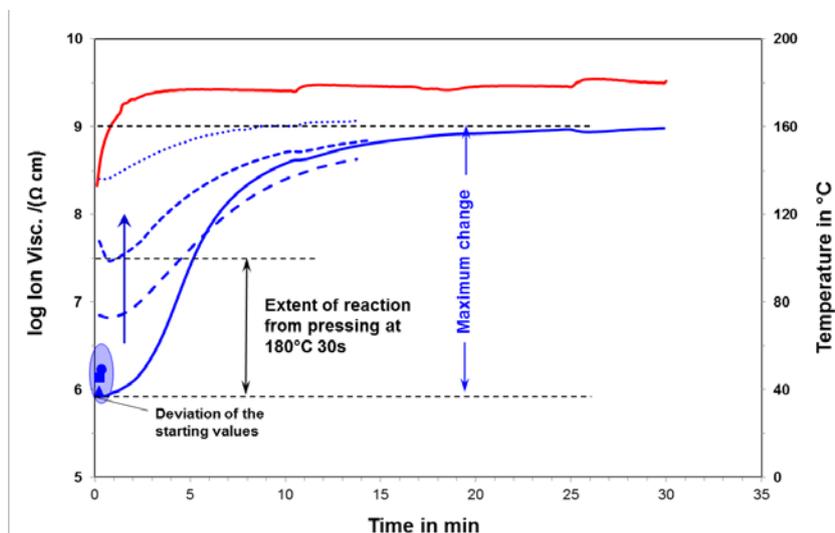


Fig. 7.

DEA at 1 kHz in pilot scale press: comparison of second-time pressing run (dashed lines) of differently short-time pressed laminates with long one-time pressing (continuous line)

Evaluation with Surface Quality Characteristics

The laminates surface properties are in general directly related to the cross-linking status of a resin. Therefore, the correlation between the ion viscosity and the extent of curing was also evaluated by surface tests of the MF laminate samples. Fig. 8 shows that ion viscosity starting minima values from short-time pressed samples are correlating well with their surface properties (acid stability and degree of gloss). This basically proves the applicability of DEA for determining the quality of MF resin based laminated wood panels. Such a second DEA run on pressed laminated samples would enable quality control by DEA.

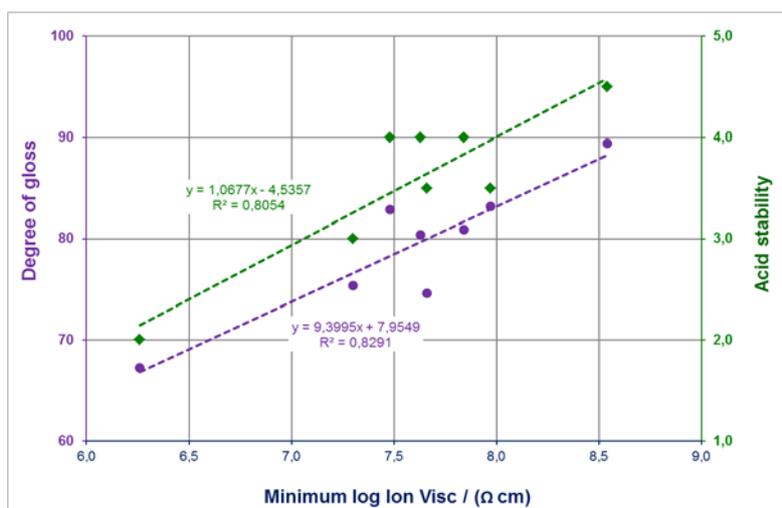


Fig. 8.

Correlation of ion viscosity starting values with gloss level and acid stability determined from industrial laminated panels

CONCLUSIONS

Cross-linking of MF resins can be determined by DEA via ion viscosity monitoring. The starting minimum ion viscosity value is higher if the sample is pre-dried or pre-cured. The ion viscosity increase can be compared with the extent of curing detected from DSC measurements. The obtained DEA data from measurements at a constant heating rate was separated into a softening and a cross-linking part. It was shown that this determined cross-linking starts at the same time as the DSC detected curing.

Nevertheless, during typical 1 minute short-time pressing of MF laminates is no significant DEA signal change detectable. We assume that cross-linking is only initiated during the typical short pressing times and a certain part of curing takes place outside the press. For detection of the curing degree of short-time pressed samples, final product samples were analyzed by DEA via a second pressing run. The obtained starting values from this subsequent pressing run correlate well with surface quality characteristics. Quality control by DEA in this form is applicable for thermoset resins with post-curing behavior.

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