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Dielectric analysis as cure monitoring system for melamine-formaldehyde laminates

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ABSTRACT

Combinations of aminoplastic thermosetting resins are used for the production of the majority of laminates. The binder's degree of curing is the key factor for the quality of laminates. Dielectric analysis (DEA), a method well-known for the curing characterization of coatings, represents an interesting way for online cure monitoring of aminoplastic resins. By measuring the dielectric properties, process-related variations in the curing behavior can be detected directly during the production.

In the present study, the applicability of DEA to papers impregnated with melamine-formaldehyde (MF) resins has been tested. Analyses were carried out during the hot pressing process, and the effects of time and temperature variation were shown. The degree of curing was determined from the changes in ion viscosity. Interestingly, the majority of the cross-linking occurs mainly after the actual hot pressing. The degree of curing determined in a second pressing/measurement cycle correlates well with the laminate's surface properties.

1. Introduction

Laminated wood panels are the commercially most relevant decorative interior elements today. The quality of lamination and particularly the surface properties of the composite product 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 process. Such an optimization is related with intensive time and material investment, particularly for research on new and emission reduced gluing systems. Basically, for any change of the resin composition, pressing parameters have to be optimized. Slight variations in processing often cause a serious impact on product performance. Thus, for the optimization of modern production processes, technologies for the online control of these processing steps are immensely asked for.

At present, dielectric analysis (DEA) is one of the most promising upcoming methods for monitoring the curing of resins. In the ideal case, implementation of this method and providing a calibration model would allow a prediction of selected properties during the production of resin based wood composites.

In principal, the materials' dielectric properties are measured by DEA as a function of time, frequency and temperature. The dielectric signals are detected by applying an alternating electrical field on the sample. The immobilization of molecular groups as a result of polymerization causes a decrease in the dielectric conductivity. This methodology, also referred to as impedance spectroscopy, is well-known for monitoring the polymerization reactions of non-aqueous, radical or polyadditive systems [1–4]. Commercial DEA instruments are available by NETZSCH-Gerätebau GmbH. In recent years, DEA was introduced in the wood glue industry and first DEA studies on polycondensating phenol-formaldehyde and aminoplastic resins were reported [5–9]. Curing of formaldehyde based resins is always based on condensation reactions and thus accompanied by the elimination of water or alcohols. Further, this elimination leads to difficult detection of the signals. In that case a superposition between water formation (increase of conductivity) and crosslinking (decrease of conductivity) is observed. In closed systems, such as injection and compression molding, eliminated water from the polycondensation mainly influences the conductivity level and for this case DEA reaches its limits for cross-linking characterization [10,11]. In contrast to such closed systems, wooden materials are

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able to absorb water and therefore the decrease of conductivity caused by cross-linking of wood adhesives can be monitored by DEA in the gluing joint.

Pretschuh et al. detected influences on DEA measurement caused by drying processes and analyzed post pressing reactions of formaldehyde based resins by DEA [9]. In 2012, a correlation between the logarithmic ion viscosity values from DEA and rheological values (DMA) was shown [12]. Nevertheless, a delay between DEA and DMA results was observed, if latent catalysts are used. In a further study, correlations of DEA signals with changes in infrared absorption and with exothermic peak integrals from DSC measurements were reported for urea-formaldehyde resins without an ionic additive [13].

Considering previous results, the objective of this present study is to test the applicability of standard DEA equipment serving as cure monitoring for typical aminoplastic resins during an industrial hot press laminating process. As a part of this study, the cross-linking behavior of melamine-formaldehyde (MF) resins was examined in detail. DEA results were proven by correlation with two alternative methods for determining the degree of curing: dynamic mechanical analysis (DMA) in a 3-point bending mode, differential scanning calorimetry (DSC) and infrared (IR) spectroscopy.

2. Theory about dielectric analysis

Dielectric Analysis of thermoset cure is described in the literature [3,4,14,15]. DEA is based on tracking dielectric changes by applying an alternating electrical field on the sample. For thin films, interdigitated electrode sensors (IDEX) with a comb structure and an electrode distance of 115 μm are mostly used. Dipoles in the material attempt to orient themselves in the electrical field and the charge carriers inside the sample are forced to move. These changes are expressed by permittivity.

Permittivity is described as a complex function of the angular frequency (Eq. (1)).

$$\varepsilon* = \varepsilon'(\omega) - i\varepsilon''(\omega) \tag{1}$$

Both, real and imaginary parts are based on ionic and dipolar changes. Depending on the applied frequency, whether ionic migration or the dipole orientation is predominant.

So, the imaginary part, also described as loss component, contains a contribution from the ion conductivity. This relation is described by the following expression,

$$\varepsilon = \frac{\sigma}{\varepsilon_0 \omega} \tag{2}$$

where ε_0 is the permittivity of the free space, ω the angular frequency and σ the ion conductivity.

By dielectric analysis, the impedance of the system is measured. The impedance presents the resistance, the ratio of voltage to the current, in an alternating field. It was introduced by NETZSCH to express this resistance as so-called ion viscosity, defined as the multiplicative inverse of the conductivity (Eq. (3)). The area of the electrodes and the distance between the electrodes are considered.

$$\text{IonVisc} = \text{bulk resistivity} = \frac{1}{\sigma} = \frac{RA}{d} \tag{3}$$

where σ is the ion conductivity (Ω^{-1} cm^{-1}), R the resistance (Ω), A the electrode area (cm^2) and d the distance between electrodes (cm).

The use of the ion viscosity or conductivity for cure monitoring and their correlations to other methods are described in literature [1,2,16,17]. These DEA values correspond well with results from infrared spectroscopy, with DSC and with rheological methods.

The relation between ion viscosity and resin viscosity is derived with the following equations [1,18]

$$\text{IonVisc} = \frac{1}{\mu[C]q} \sim \frac{1}{\sigma} \tag{4}$$

$$\mu \sim \frac{1}{\eta} \tag{5}$$

$$\text{IonVisc} = \frac{1}{\sigma} \sim \eta \tag{6}$$

where μ is the ion mobility, $[C]$ the mobile ion concentration, q the charge of an ion and η is the viscosity.

By performing DEA measurements with a NETZSCH curing monitor equipment, the values of ion viscosity or ion conductivity and also permittivity values, can be monitored at a defined frequency range.

3. Materials and methods

MF impregnation resin Kauramin® 773 was obtained as a powder from BASF. MF impregnated papers were prepared by inserting the paper for 10 s in aqueous 50% MF Kauramin® solution (without curing agent) and pre-drying at 130 °C. The typical industrial laminates A and B were provided from FunderMax.

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 115 μm. With standard equipment for curing characterization, measurements can be carried out at a common frequency spectrum from 10^1 to 10^4 Hz (range of ionic conductivity between 10^{-4} and 10^{-11} S cm^{-1}). An overall impedance spectrum cannot be measured.

For each measurement the sensor is mounted on the sample and the alignment is transferred into a laboratory hot press for isothermal measurements. Aqueous MF glue without curing agent and MF impregnated papers were analyzed in laboratory scale between wood veneer joints at the minimum possible setting of 10 N cm^{-2}. MF impregnated papers and typical industrial laminates were further analyzed during hot pressing on a 16 mm particle board at 150 N cm^{-2} (laboratory press) and at 294 N cm^{-2} (pilot scale press), respectively. For experiments in pilot scale the sensor was fixed on the impregnated laminate on the top of a sandwich construction (stabilizing layer, particle board, underlay paper and decorative laminate). The observed ion viscosity is a multiplicative inverse of the ion conductivity.

Enthalpy values from exothermic curing peaks were determined by DSC measurements on MF impregnated and pre-dried papers for a comparison with ion viscosity difference values. The experiments were performed in hermetic pans at a constant heating rate of 20 K min^{-1} using a TA Instruments DSC Q20.

The ATR infrared spectra of laminate samples were recorded on a Perkin Elmer ATR FT-IR at a constant heating rate of 3 K min^{-1}. The spectrum was measured in ATR-mode (golden gate single reflection ATR) at 4 cm^{-1} resolution with 10 scans per single measurement. For calculation of the intensity, the absorption band area of the hydroxymethyl group at 1000 cm^{-1} was related to the intensity of the triazinyl band area at 810 cm^{-1} [19].

Measurements for the correlation of DEA and DMA data were carried out in 3-point bending mode of a TA Instruments DMA Q800 at a constant heating rate of 3 K min^{-1}. The industrial laminate sample was mounted between two beech veneers, fixed in 3-point bending mode with 3 N pre-force and 250% force track, and stressed with an oscillation frequency of 1 Hz at an amplitude of 40 μm. For DEA measurements, a Mini-IDEX Sensor was placed between the laminate and the veneer. DMA and DEA experiments