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A New Methodology to Evaluate the Cure of Resin-Impregnated Paper for HPL

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This paper presents a study on the curing conditions of several resin-impregnated papers and its impact on the performance of HPL (high-pressure decorative laminate). A new methodology for evaluating the bond strength development between the different layers of a HPL(overlay, decorative, and kraft papers) was developed using ABES (Automated Bonding Evaluation System) equipment. The proposed method can be applied to the study of the curing step of the different impregnated paper and the development of bonds between them (overlay paper on decorative paper, decorative paper on kraft paper, and kraft paper on kraft paper) trying to simulate the hot-pressing of an industrial HPL. This will permit to establish a more adapted temperature gradient in hot-press in order to achieve the same curing rate for all layers and provide a good final overall product quality.

KEYWORDS Adhesion by chemical bonding; Adhesives for wood; Composites; Mechanical properties of adhesives

1. INTRODUCTION

High-pressure decorative laminates (HPL) are a multipurpose, high strength, and value-added surface material for use in construction (facades, walls, and flooring) and furniture sectors. A standard HPL consists of layers of cellulosic fibrous material (normally paper) impregnated with thermosetting resins (usually melamine-formaldehyde and phenol-formaldehyde), bonded together by a high-pressure process and normally are used for surfacing wood based panels. The high-pressure process consists on the simultaneous application of heat (temperature≥120°C) and high-pressure (specific pressure ≥5 MPa), and intends to enable the flowing and subsequent curing of the thermosetting resins to produce an homogeneous, non-porous material with increased density (≥1350 kg/m) and with the required surface finish [1]. A usual build-up (see Fig. 1) includes a set of kraft papers impregnated with a phenolic resin to provide physical and mechanical resistance to HPL, a decorative sheet impregnated generally with melamine-formaldehyde resin and an overlay paper impregnated with a melamine-formaldehyde resin to provide resistance to abrasion.

In the last years the production of HPL has increased and new products are being launched, such as: HPL produced with new impregnation resins, HPL with new functionalities (chemical resistance, wear resistance, UV resistance, *etc*.), compact HPL (high thickness).

New impregnation resins have been used in HPL such as melamine- formaldehyde resins copolymerized with different monomers, resins from different chemical nature as acrylic, polyurethane, *etc*., and hybrid resins combining the melamine-formaldehyde resins and other kind of resins usually used in coatings. New additives were also introduced to provide new functionalities to HPL, as UV resistance, chemical resistance, dirt repellence, self-healing, anti-microbial, *etc*. Since these resins and additives have different drying and curing behavior, the introduction of new resins and the incorporation of additives lead to new process optimization problems. The HPL production involves several operations, such as the impregnation (resin content, speed, temperature) and the hot-pressing (time, temperature, pressure schedule), whose parameters are heavily dependent on resins curing dynamics.

This optimization problems increase the interest on the development of a novel methodology to evaluate the cure of the resin-impregnated paper.

The surface quality of HPL can be evaluated, according to the current standards, by several methods as the resistance to scratch, abrasion, and stain resistance, according to EN 438-2. A few papers have addressed the study of the impact of the manufacturing variables (paper type, raw paper weight, resin content, impregnation/coating process) on the surface quality [2, 3]. The composition and structure of paper have a great influence on surface quality. The presence of fatty matter (extractives) and inorganics fillers together with structural anisotropy of paper confers the difference in affinity of the face and backside of papers towards phenol-formaldehyde resins [4]. The impregnation stage is also important since the resin pick up will also affect the surface quality. As resin pick-up increased, abrasion and scratch, staining and cigarette burns resistance are improved. However, the pressing stage is still the most important process in the production of HPL. During this process the resin flows and cures between layers, thus creating a cross-link and promoting the consolidation of the final laminate [4].

To evaluate the resin cure in HPL manufacturing, the Werzalit method has been used in industry. This method permits to determine the time that an impregnation resin takes for hardening. A rectangular test piece of 9.5x6.0 cm of impregnated paper is immersed in a silicon oil bath at 100°C and the hardness is measured along the time. The curing time is the time in which the hardening of the sample is 95% of the maximum hardness. Other methods are reported in the literature, as DSC (differential scanning calorimetry). Although this technique is a common technique to evaluate the degree of chemical curing of thermosetting resins, it has been little explored for these materials to evaluate the extension of cure of kraft paper impregnated with phenolic resin [5]. The near-infrared spectroscopy (NIRS) was also success- fully used by the same authors [5] to predict the extent of phenolic resin curing into saturating kraft paper in a non-destructively, cheap, and fast way. Although these methods allow the estimation of the degree of "chemical curing," they are not able to predict the bond strength development between layers during the industrial hot-pressing of HPL.

ABES (Automated Bonding Evaluation System) is a powerful and versatile technique for evaluation the "mechanical cure," allowing the determination of the shear strength as a function of resin type, catalytic system, resin load, cure temperature, time, and substrate [6]. It allows the determination of the isothermal strength development rate of the bond to be characterized at temperatures ranging between ambient and 260°C and may be used to explore many types of bonding systems including those that are thermosetting, as urea-formaldehyde, melamine-urea-formaldehyde and phenol-formaldehyde [7–9] and thermoplastic as poly(vinyl acetate) [10]. This instrument may also be used as a platform for a diversity of hybrid experiments related to the characterization of diverse aspects of adhesion [11].

For ABES testing, a specimen consisting on a pair of relatively thin adherent strips (generally wood veneer) is used, the adhesive is applied at the end of one strip, and the two strips are overlapped to form miniature bonds typically measuring 20 x 5 mm. The alignment of the lap shear samples can be easily ensured by the equipment. The specimen is put in the device and pressed in a miniature hot-press. Immediately after curing to a preselected extension (pressing time), the press opens and the lap-shear specimen is tested in shear mode (the system is digitally controlled and pneumatically driven). Tensile load and pulling head movement are monitored until failure occurs (see Fig. 2) [12]. Considering the fast and easy sample preparation as well as the possibility of a real-time monitoring of bond strength development under the same hot-pressing conditions used in industry, ABES equipment was selected as the tool for studying the cure of impregnated papers for the production of HPL.

So, the main objective of this work was to establish a new methodology for the evaluation of impregnated paper cure using ABES apparatus, trying to simulate the hot-pressing of an industrial HPL.

2. MATERIAL AND METHODS

2.1. Materials

For ABES tests, the impregnated papers for high-pressure laminates (kraft paper, decorative paper and overlay paper) were provided by SIR (Sonae Indústria de Revestimentos, SA, Maia, Portugal) and beech veneer strips were supplied by Sonae Indústria, PCDM, SA (Mangualde, Portugal).

During the impregnation, the different resins were applied in an industrial impregnation line, in one or two steps. The raw paper is immersed in a bath containing the impregnation resin, becoming soaked and the excess of resin is mechanically removed from the web by the action of squeezing rolls. The impregnated paper is then dried which cures resin at the surface of the paper. It can also be immersed in a second bath called coating, then dried and finally cooled down. The resin is partially cured and the cure is completed during the hot-pressing operation that can be performed in another industrial plant. In the production of HPL, several plies of different kind of papers (kraft, decorative, overlay) are superposed and then pressed in a hot-press to consolidate the mat into a laminate.

In this study, two types of kraft papers, four types of decorative papers and four types of overlay papers were used. The different samples were collected at the industrial sites and conditioned in the lab (20°C, 65%) during two weeks and then cut to size.

2.2. Methods

The different papers (kraft, decorative, and overlay) where cut into 117x20 mm strips using a pneumatically driven sample cutting device used for standardized ABES sample preparation. Due to the different mechanical properties of the impregnated papers (kraft, decorative, and overlay) and their different thickness, several sample configurations were selected. Only the three types of bonds that occur on HPL were tested (overlay paper over decorative paper, decorative paper over kraft paper, and kraft paper over kraft paper).The ABES test was performed at temperatures of 140°C and standard mode (after the pressing time was elapsed, bonds were immediately pulled without cooling). The standard overlap area of the two strips was always 100 mm^2 (20 x 5 mm).

3. RESULTS AND DISCUSSION

3.1. Sample Configuration

3.1.1. KRAFT PAPER

Several preliminary studies have been carried out to determinate the number of sheets of kraft paper needed to avoid the sliding of the specimens on the grips during the pull-off operation. During those preliminary tests, it was noticed that the grips could not hold the kraft paper and that, at the higher temperatures, the kraft paper might glue to the pressing plates.

In order to overcome those problems, it was decided to apply 0.5 mm thickness wood veneers strips on the back of the kraft paper. This veneer strips would act as support, for the grips, and as a protection, for the press plates. This sample configuration was coded as WK+KW indicating at the same time the use of two strips of wood (W) and two of kraft paper (K) and the study of the bonding between two kraft strips (K+K) [Fig. 3(a)].

3.1.2. DECORATIVE PAPER

Decorative paper (melamine impregnated) is very brittle and if it is cut into samples of 117x20 mm and tested, it would broke at the grips. Therefore, it was decided to cut the melamine paper into samples of approximately 20x20 mm, which were then fixed with adhesive tape to kraft paper strips of 117x20 mm and backed with the same size beech wood veneer strips. The kraft paper would act as tractor, for the shear test, and the wood veneers behave as support for the grips, and as protection, for the press plates.

This configuration was coded as WKD+KW indicating at the same time the use of two strips of wood (W), two of kraft paper (K) and one strip of decorative paper, and the study of the bonding between decorative paper and kraft paper (D+K) [Fig. 3(b)].

3.1.3. OVERLAY PAPER

The overlay paper is very thin and very brittle (high amount of melamine resin), so it was out of the question to cut it into specimens of 117x20 mm. Therefore, the overlay paper was also cut into samples of approximately 20x20 mm, which were then fixed with adhesive tape to pieces of 117 20 mm of decorative paper. The set was then backed by beech wood veneer strips. The wood veneers would act as tractor, for the shear test, as support, for the grips, and as protection for the press plates.

This configuration was coded as WDO+DW indicating at the same time the use of two strips of wood (W), two of decorative paper (D), and one strip of overlay paper (O) and the study of the bonding between overlay paper and decorative paper (O+D) [Fig. 3(c)].

3.2. ABES Results Analysis

The mathematical model proposed by Martins et al. [12] [Equation(1)] was applied to the experimental data. This model was established for the study of the dynamic of curing reactions of urea-formaldehyde (UF), melamine- formaldehyde (MF), and phenol-formaldehyde (PF) resins and describes the time evolution of the shear strength (τ). The method has three para- meters, which can be obtained by data fitting,— τ_∞ maximum shear strength In Figs. 4–6 the bond strength developments in function of time is presented for the different configurations/impregnated papers is presented in both raw experimental data and fitted model. Globally the different impregnated papers have very different curing behavior.

$$\tau = \frac{\tau_\infty}{1+\alpha}\left(\alpha + \tanh\left(\frac{t - t_{gel}}{\lambda}\right)\right);\ \alpha = \tanh\left(\frac{t_{gel}}{\lambda}\right) \quad (1)$$

There is not a major difference between the different *kraft* papers (Fig. 4), but one of the decorative papers (Decor-C) has a lower curing rate (Fig. 5), whereas one of the overlay papers (Overlay-D) has a much higher curing rate (Fig. 6). So, it is possible to conclude that they should not be used in HPL production, since there is a great difference in the reaction rate, which can lead to surface defects.

From the analysis of Fig. 7, where the estimated t_{gel} (gel time) of the different impregnated papers is presented, we can easily observe that, with the exception of the decorative paper Decor-C, there is an increase on t_{gel} along the thickness of HPL from the surface (overlay) to the core (kraft). A pressing system more adapted to a HPL produced with these impregnated papers (with the exception of Decor-C) should take into account this behavior and should impose a specific temperature gradient (higher temperature in the core and lower in the faces).

4. CONCLUSIONS

The proposed methodology can be applied to the study of the curing step of the different impregnated paper and the development of bonds between them (overlay paper on decorative paper, decorative paper on kraft paper, and kraft paper on kraft paper). The use of the proposed sample configurations (WK+KW, WKD+KW, and WDO+DW) enables the ABES technique for testing impregnated papers.

The tested papers, with the exception of the decorative paper Decor-C, can be used for the production of HPL if the pressing system can impose a temperature gradient (higher temperature on the core and lower on the faces). When an overlay paper (Overlay-D) is used, the temperature gradient has to be slightly modified.

This methodology can help to establish a more adapted temperature gradient in order to achieve the same curing rate for all layers of HPL.

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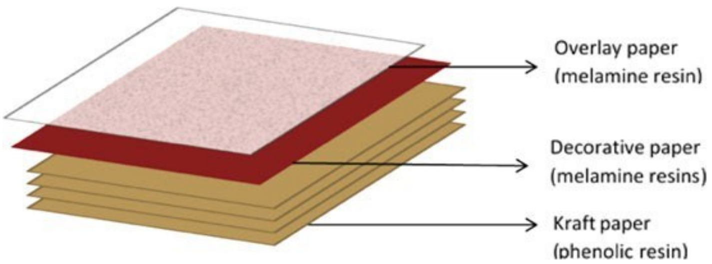

FIGURE 1 Typical assembly of HPL.

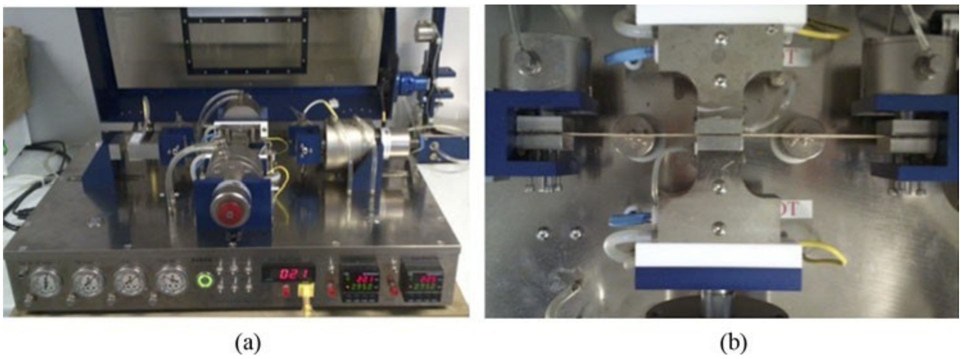

FIGURE 2 ABES equipment: (a) front and (b) top view.

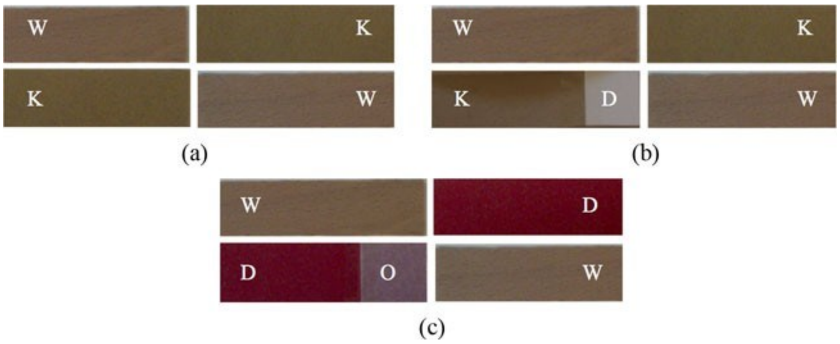

FIGURE 3 Sample configuration for ABES testing: (a) WK+KW, (b) WKD+KW, and (c) WDO+DW.

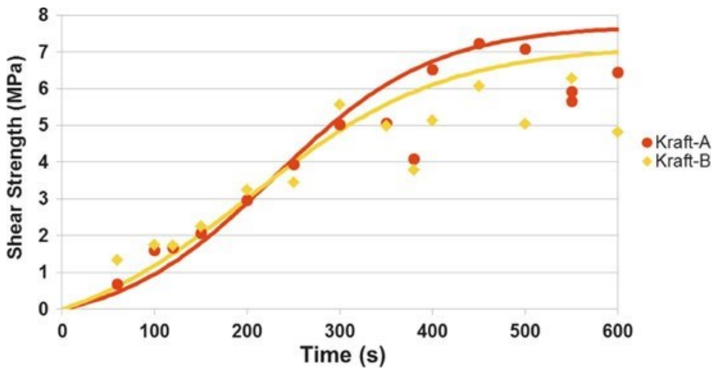

FIGURE 4 Isothermal strength development—kraft paper.

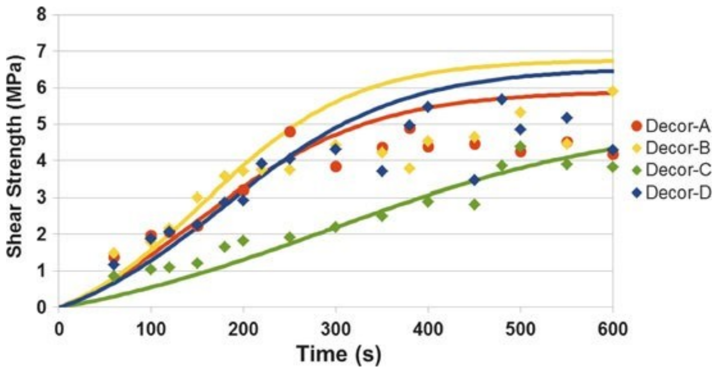

FIGURE 5 Isothermal strength development—decorative paper.

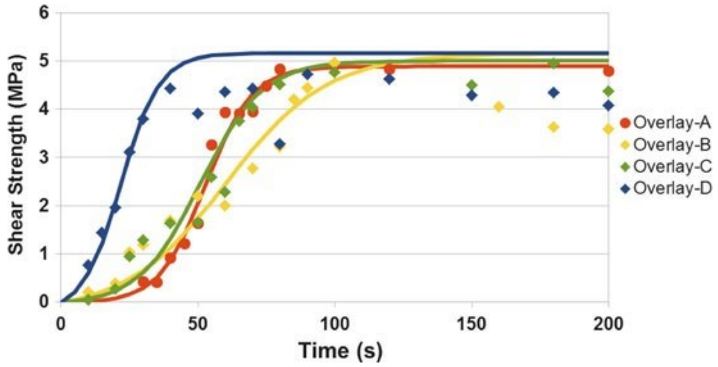

FIGURE 6 Isothermal strength development—overlay paper.

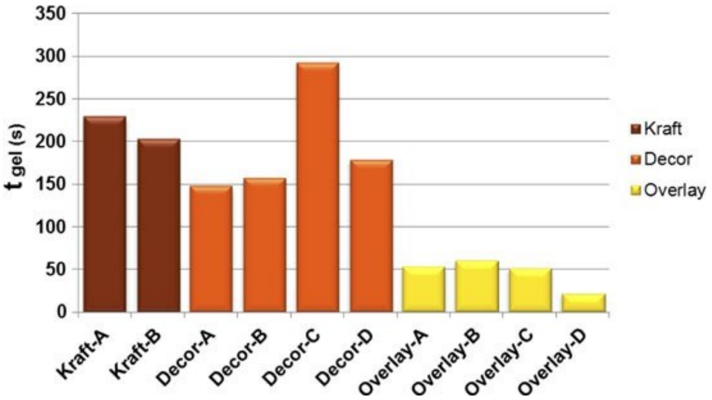

FIGURE 7 Gel time for different impregnated papers.