TESTING

New test method for the characterization of paper/melamine reactivity

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ABSTRACT

The disc cure test was presented by James Larkin at the TAPPI 19th Plastics Paper Conference in 1964. At the time it was identified as "A simple method for measuring the cure speed of thermosetting resin/paper combinations." The disc cure test does not account for the aqueous melamine interactions with the salts contained in decorative papers. We are proposing an improved test procedure that accounts for the interactions of the inherent paper chemistries with the melamine chemistry. This test uses pressure differential scanning calorimetry to characterize the reactivity of decorative papers treated in an aqueous melamine solution.

Application:

This test procedure can be used as both a research and development tool, to better understand the interaction of the paper chemistry with the aqueous melamine chemistry, and as a quality control/quality assurance tool, to monitor reactivity from paper to paper (and lot to lot) as a routine incoming decorative paper analysis.

THE DISC CURE TEST WAS FIRST presented to the decorative laminate industry in 1964 by James Larkin in the paper "A simple method for measuring the cure speed of thermosetting resin/paper combinations" *(1)*. This paper described the use of a powdered melamine resin placed on top of the paper to be analyzed. The combined sample was placed in a folder of foil and then pressed at 284°F and 1000 psi for selected time periods. The resulting samples were then immersed in boiling water for 5 min and then dried and examined for whitening. (A variation of the test is to immerse the samples in a boiling water/Rhodamine B dye solution for 3 min, after which they are dried and examined for surface color change due to the dye.) Undercured samples showed severe whitening (or a color change due to the dye). This method has stood the test of time, as is evident by its length of service in the industry.

BACKGROUND

The disc cure test yields valuable information. However, it uses powdered melamine resin, which does not completely reproduce the interactions that occur between the paper chemistry and the aqueous melamine chemistry during the standard treating process.

Normally the processes related to manufacturing decorative papers impart a number of chemistries to the finished paper. These may include any or all of the following *(2, 3)*:

- A cleaning process of the pulp that can use either a bleaching process or a hydrogen peroxide process
- Soda ash (sodium carbonate) and alum (hydrated aluminum sulfate) added at the paper machine to control pH
- Wet-strength resins added to the pulp
- Fillers, pigments, wetting agents, defoamers, and other additives used for particular paper requirements.

These additives may deposit certain salts onto the finished paper that, upon treating in an aqueous solution of melamine/formaldehyde, can affect the activity of the matrix.

At the TAPPI 1994 Plastics Laminates Symposium, Schoenberg presented a paper discussing the use of pressure differential scanning calorimetry (PDSC) for monitoring the effects of paper interactions during the treating process *(4)*. Using this initial work, we have developed a testing technique that allows us to characterize the interaction of aqueous melamine and the inherent paper chemistries.

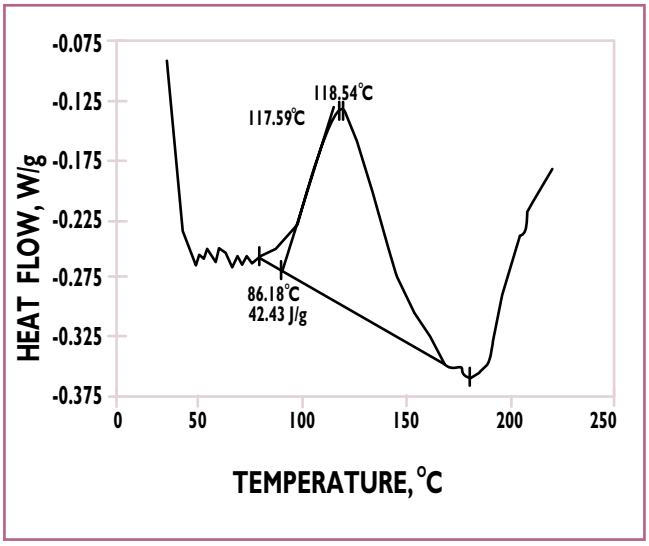
TESTING TECHNIQUE

Sample preparation

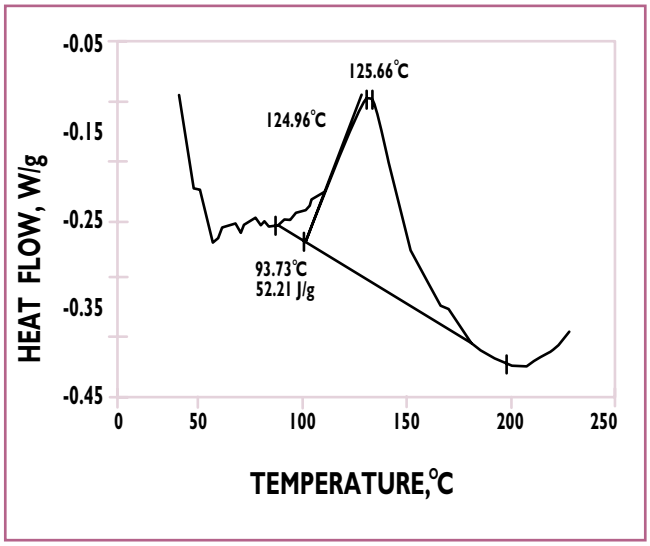
This test procedure features a noncatalyzed, melamine/formaldehyde aqueous resin solution at approximately 45% water content. The paper to be tested is cut into 2 x 6 in. strips, and the lower 4–5 in. are dipped into the resin solution. The paper sample is allowed to degas (fully wet out) in the resin and then is drawn through two glass rods to remove the excess resin. After each sample is drawn, the glass rods must be cleaned using an isopropanol/water solution. The same melamine solution is not to be used for more than two different paper samples. The hand-dipped paper is air dried in a forced-air hood for 2–3 hours. After air drying, the samples are placed in a 24% relative humidity (RH) chamber (containing acetic acid, potassium, salt, and water) for at least 16 hours (to reach equilibrium) prior to testing. Sample must be tested within 75 hours from the time of saturation.

PDSC testing

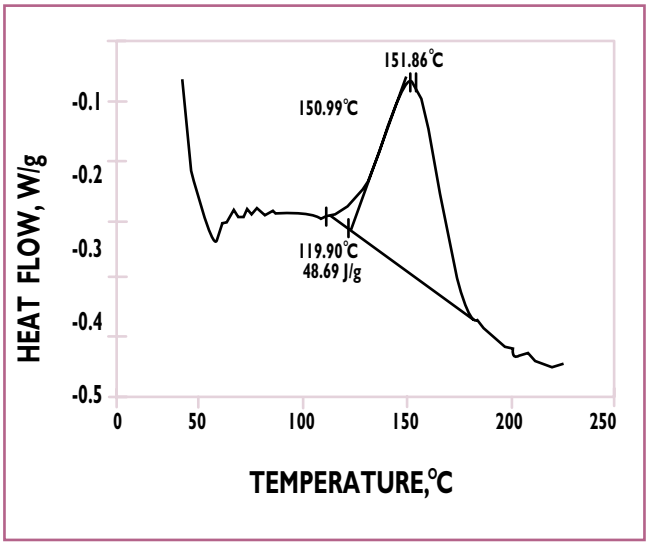
Using a cork borer with an outside diameter of 0.172 in. (4.41 mm) and an inside diameter of 0.1385 in. (3.54



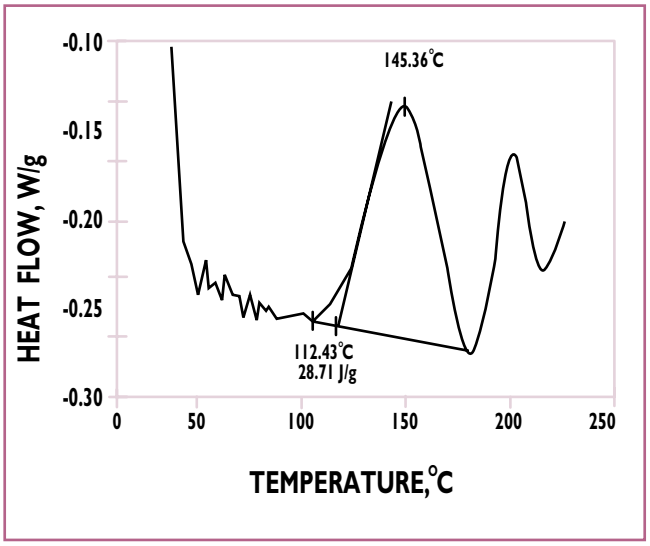
1. Fast HPL decorative paper with aqueous melamine air-dried and stabilized–Pioneer proprietary resin



2. Fast HPL decorative paper with aqueous melamine air-dried and stabilized–BTLM 2826 resin



3. Slow HPL decorative paper with aqueous melamine air-dried and stabilized–BTLM 2826 resin



4. Slow HPL decorative paper with aqueous melamine air-dried and stabilized–Pioneer proprietary resin

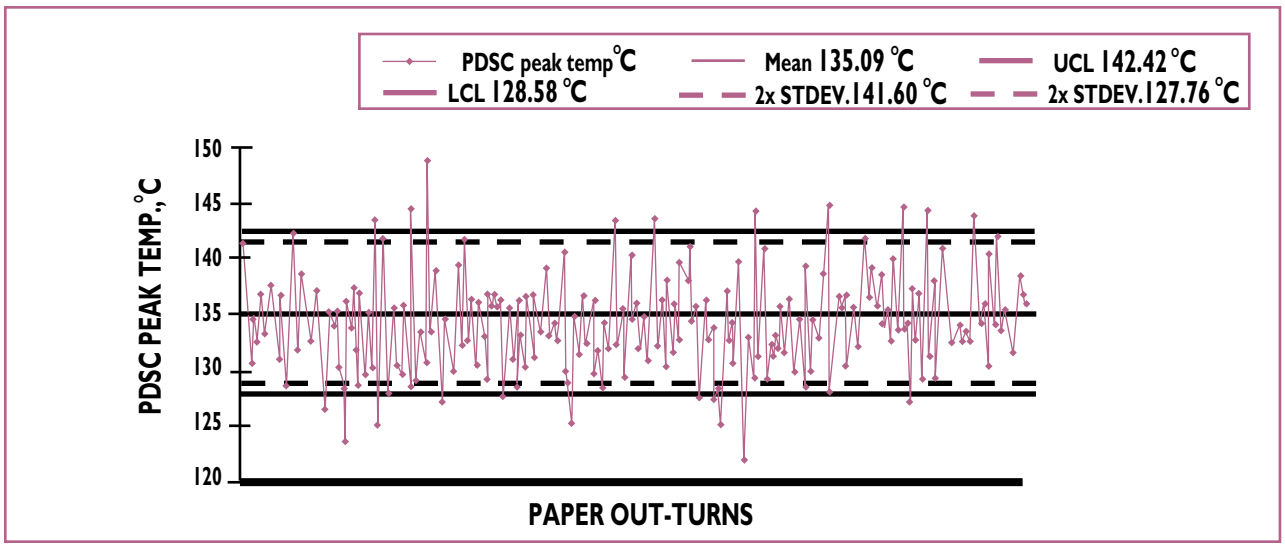
mm), cut out three to six discs from the sample to be tested. The combined weight of these discs should be 9–12 mg. Place the sample discs in the bottom of an anodized aluminum hermetic-type differential scanning calorimetry (DSC) pan to provide maximum surface contact of the sample with the pan bottom. Use a pin with a diameter of 0.02 in. (0.53 mm) to make a hole in the pan lid. Hermetically seal the pan, and place a glass ball with a diameter of 0.117 in. (2.97 mm), weighing 35.8–36.4 mg, over the hole. Prepare the reference pan with the same diameter pin hole and glass ball. Run the PDSC thermal scan at 800 psi, 10°C/min from ambient temperature (approx. 25°C) to 230°C.

PDSC data analysis and verification

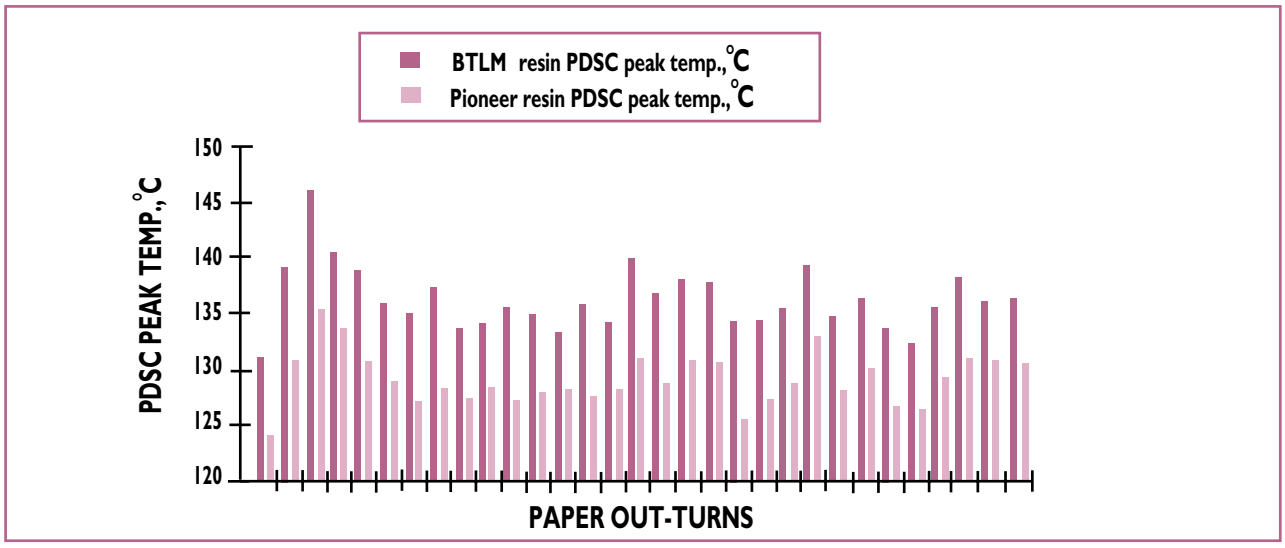
Upon completion of a PDSC run, integrate the exotherm peak, and calculate the onset temperature, peak temperature, and enthalpy. Data are valid when the exotherm peak temperature is easily determined. The curve will have a smooth, rounded peak, and the baseline will have little or no discernible noise **(Fig. 1–4)**. The sample needs to be rerun when the peak apex is not easily defined due to any shoulders or noise in the top of the curve.

RESULTS

Since February 1995, Pioneer Plastics has been running this reactivity testing on all incoming out-turns of decorative paper. **Figure 5** is a control chart of the resulting data from February 1995 to May 1996. We have been able to correlate the postform-



5. HPL paper out-turn reactivity study—2/95–5/96



6. HPL paper out-turn reactivity study—BTLM resin vs. pioneer resin

ing and hot-water-resistance performance of samples to their data location on this control chart. This has allowed the paper vendors to better understand the requirements of Pioneer and reduce the variation from paper to paper. These data were generated using a noncatalyzed resin chemistry that is proprietary to Pioneer.

When we decided to offer this test procedure to the rest of the industry, we identified a supplier of melamine/formaldehyde (M/F) powder resin that was analogous to the types of M/F ratios that would relate to those used in the decorative laminate industry. BTLSR Toledo, Inc., has a resin, MF860 (referred to as BTLM resin in the figures), that we have used to correlate to the proprietary resin used for the development of this test. We made a 55% solids solution of this resin in water and followed the same procedure that was previously discussed. **Figure 6** shows a correlation chart of the reactivity results between the internal resin and the BTLSR resin. **Figure 7** is an example of a highly reactive paper and a slow paper. As can be seen by the breadth of these data, there is a significant difference between the reactivities of these papers.

DISCUSSION

Not only has this test helped Pioneer predict the performance of the paper in production, but it has allowed us to give valuable feedback to the paper suppliers relating to the inherent reactivity of the paper. We have also found that papers with similar disc cure numbers may have

KEYWORDS
Amine polymers, calorimetry, chemical properties, composites, curing, decorative papers, laminated plastic, laminates, polycondensates, polymelamines, reactivity, specialty papers, test methods, thermal measurement, thermosets.

significantly different reactivities as measured with this test. We are offering this test to the industry in hopes that, with input from the various laminators and paper vendors, we can make this a universal test. Pioneer believes that the data generated from this test procedure, when used with other test data (e.g., hot extract pH, disc cure, etc.), increase our understanding of the interactions of paper and aqueous melamine resin chemistry. This has gone a long way to better understanding and controlling our process and product. **TJ**

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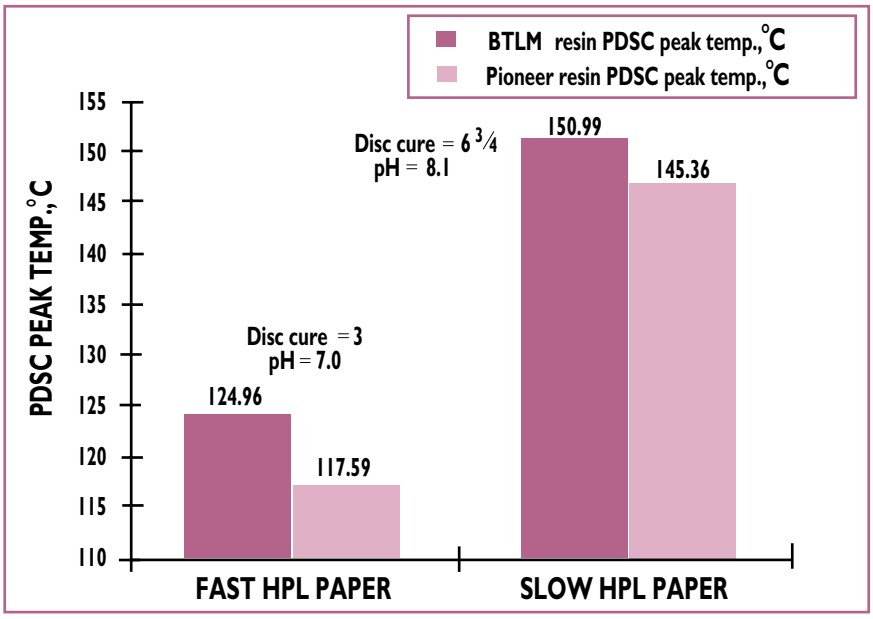

7. HPL papers with fast and slow reactivities—BTLM resin vs. pioneer resin

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3. Genco, J., *Proceedings of the 34th Annual University of Maine Pulp and Paper Summer Institute,* University of Maine, Orono, ME, 1993.
4. Schoenberg, A., *TAPPI 1994 Plastic Laminates Symposium Proceedings,* TAPPI PRESS, Atlanta, p.149.