Temperature and Reactant Injection Effects on the Bonding Dynamics of Thermosetting adhesives

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ABSTRACT

The bonding speed of adhesives within bio-composite materials during hot pressing critically influences manufacturing speed and efficiency. Matching the reactivity of adhesives to pressing processes and raw materials requires specific information on the responsiveness of adhesives to thermal and chemical environments that occur. The Automated Bonding Evaluation System (ABES) enables such effects to be characterized quickly and accurately in the laboratory. Derived data is directly and practically useful for those developing adhesives and those using them in industrial pressing operations. The results of a range of investigations relevant to adhesion in the formation of present and future bio-composite products are summarized in this paper. These include 1) the effect of temperature on the strength development rates of UF-to-wood bonds 2) the strength enhancement that results from rapidly cooling partially cured PF bonds prior to their being tested 3) the thermal damage of UF adhesive bonds as a function of temperature and time and its potential impact on press cycles and composite performance; 4) the effects of spread rate and moisture on the isothermal bonding rate of pMDI adhesives; 5) the influence of the sequential application of reactive chemicals on the strength development of PF bonds – these were sequentially exposed first to a cell wall softening agent (ammonia) and then to a room temperature catalyst (methyl formate).

INTRODUCTION AND BACKGROUND

The Automated Bonding Evaluation System (ABES) technique and associated instrument (Patent: Humphrey 1993) allows the strength development characteristics of a diversity of adhesive types to be explored. The laboratory instrument provides a means of efficiently evaluating the bond strength development compatibility of adhesives for many industrial manufacturing operations.

The system allows the isothermal strength development rate of adhesives to be characterized at temperatures ranging from ambient to 250^{o}C. ABES may be used to explore many types of bonding system (including thermosets, thermoplastics, activated thermosets, powders, isocyanates, epoxies), as well as the effects of injected chemicals on adhesion. An overview of the main bond forming unit and control module is shown as Figure 1.

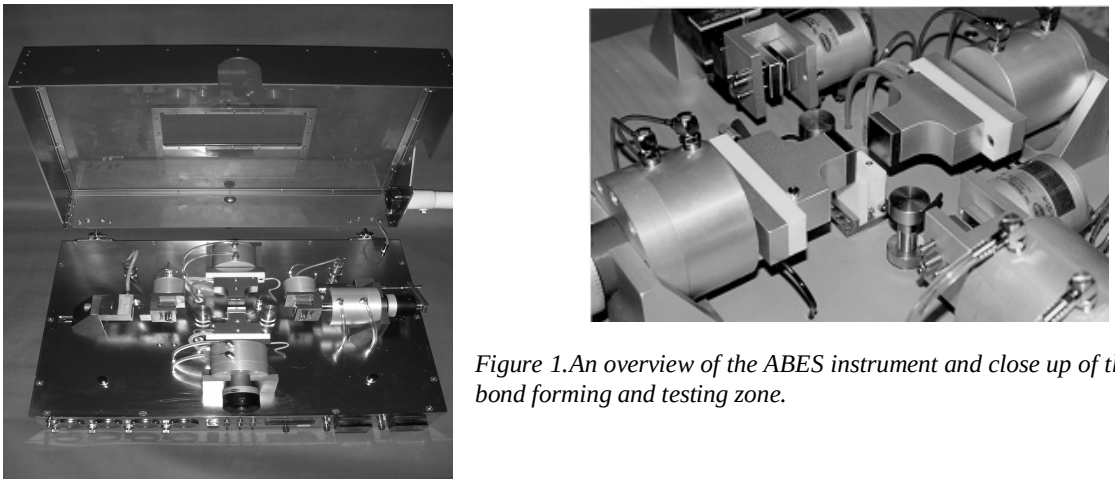
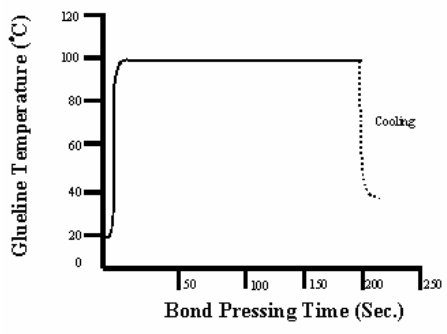


Figure 1.An overview of the ABES instrument and close up of the bond forming and testing zone.

Small (typically 20 mm x 5 mm) adhesive bonds are precisely formed in the system under highly controlled conditions of temperature, pressing load, and time. Immediately after each bond is cured to the required level, it is tested to destruction in shear mode. Tensile load and pulling head movement (sample elongation) are monitored digitally during bond pulling, and strength (overlap-area-corrected peak shear load) is calculated.



By using relatively thin (or heat diffusive) substrate strips, target temperature is achieved very shortly (typically 8 seconds) after the beginning of bond forming periods (where the heated blocks close on the overlap). In this way, near-isothermal bond strength development may be achieved shortly after the beginning of bond forming periods; this is necessary for adhesion kinetics studies described below. A typical bond-line heating curve is shown as Figure 2; this one is for wood substrates of 0.7 mm thickness pressed at 100^{o}C.

Figure 2. A typical glue-line heating curve (for 0.7 mm thick maple with ABES set to 100 ^{o}C).

Rapid repetition of the bond forming and testing procedure for a range of pressing times (while holding pressing block temperature constant) enables isothermal bond strength accumulation with time to be explored and plotted. Each point on such a plot therefore corresponds to a similar glue bond that has been cured under controlled conditions of temperature, time and pressure and immediately thereafter automatically pulled to measure its accumulated shear strength. Repeating *this* procedure for a number of different pressing temperatures enables a family of such isothermal bond strength accumulation plots to be constructed. Failure mechanisms may also be explored for the variously cured bonds using SEM or related analytical techniques.

The adhesive application method employed depends on the objectives of the study being undertaken, but a precision micro-spray system specially developed for ABES is most often employed. This enables spread rates from 2 grams/m^2 up to saturation with some control of droplet size. Powdered adhesives may be precisely applied using a system incorporating miniature sonically agitated sieves.

A SELECTION OF REPRESENTATIVE RESULTS

A typical set of bond strength development data for a UF adhesive

A typical set of strength development data for a thermoset (in this case a urea formaldehyde adhesive used in panel manufacture) is shown in Figure 3 (left). This, as for most (but not all) types of thermosetting adhesive, exhibits nearly linear isothermal strength development up to quite high levels of cure, and linear regression may therefore be applied. The slopes of the regressed lines represent the bond strength development *rates* corresponding to the pressing temperatures employed. Plotting these rates against forming temperature provides a very useful fingerprint reflecting the reactivity of the adhesive-substrate combination (Figure 3, right).

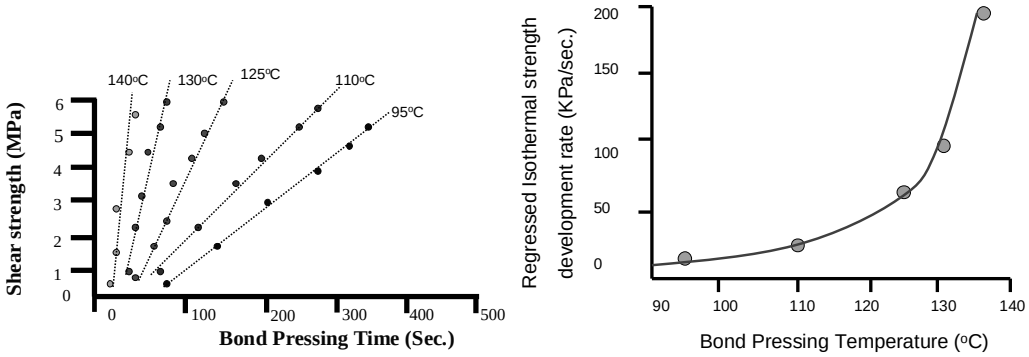


Figure 3. A typical set of isothermal strength development plots for UF adhesive-to-maple bonds (left), with a derived plot of regressed bonding rate against temperature (right).

The technique may be used to resolve the effects of small differences in adhesive formulation. Such information is highly useful in tailoring adhesives to particular manufacturing operations. For a typical adhesive kinetics study such as the one above, about eight bonds are usually needed to ascertain a well-defined bonding curve per temperature, and four or five temperatures are selected (about 40 bonds in all). Such an evaluation may typically be executed within half a day. For many adhesive screening studies a less complete testing regimen is often sufficient; an indication of the relative speed of adhesives may, for example, often be ascertained by using just one pressing temperature. The most promising formulations would then be fully evaluated. Such an approach offers a highly efficient and specific alternative to many costly pilot lab or mill board trials.

Using ABES data in models of industrial panel pressing

To help demonstrate the significance of bonding speed-versus-temperature curves like the one in Figure 3 (right), it will be used here to estimate the development of bond strength that occurs in a simulated industrial continuous MDF press where internal temperatures change with time (Humphrey, 1997; Bolton, et al, 1989; Thoemen and Humphrey, 2003). A predicted cross-sectional distribution of temperature along the length of the press is shown as Figure 4 (left) along with a corresponding predicted bond strength development curve (Fig.4, right). The bonding curve has been derived by fitting the curve of Figure 3 (right) with an exponential function and then combining it with the temperature data of Figure 4 using numerical methods.

The accumulation of bond strength is shown here in order to provide a qualitative indication of the effect of adhesive curing characteristic on industrial bonding behavior. Such strength development is important in affecting the attainment of panel integrity (the ability of adhesive

bonds to counter the destructive contributions of internal fluid pressure and residual stress within the compressed wood fibres or particles) when the panel exits the press.

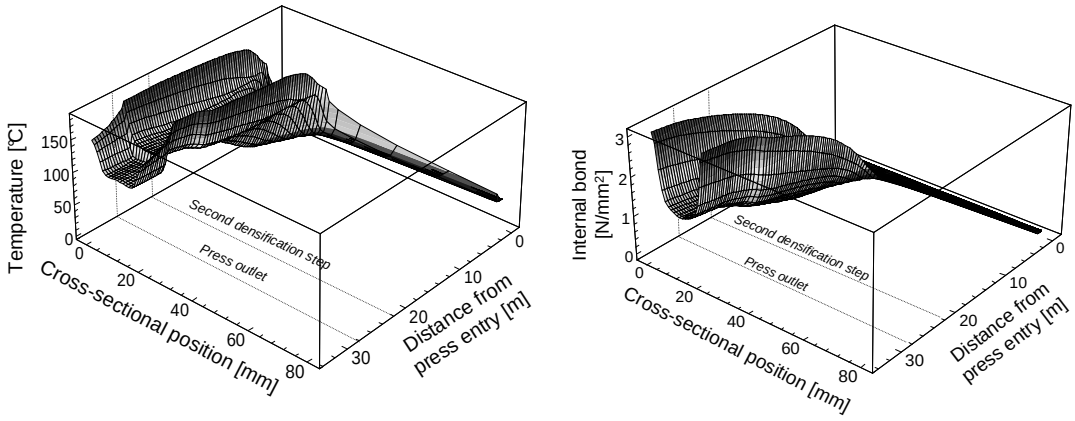
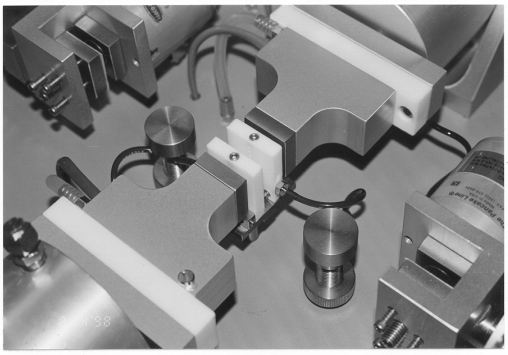


Figure 4. Simulated temperature (industrially verified) and derived bond strength distributions through the thickness of a UF bonded wood composite (MDF) as it passes through a continuous press running at 160°C (initial mc of 8% and final density of 650 kg m^{-3}).

Exploring the thermal properties of partially cured adhesive bonds

Provision is made on ABES for computer controlled cooling of bonds immediately prior to their being pulled. This is achieved with a pneumatically driven and computer controlled spring-loaded PTFE cooling head (Fig. 5). This function enables ABES to be used to explore the thermoplastic characteristics of adhesive systems, including those that are predominantly thermosetting (Humphrey, 1994, 1996, 1997).



Rapidity of cooling is necessary to minimize further curing prior to testing (typically affected within 3 seconds), while accurate control of the extent of cooling from a wide range of starting temperatures is necessary to fully characterize thermal effects (typically within 1.5°C of target values).

Figure 5. Schematic diagram of the air-jet cooling head in the activated position

A sample set of strength development data for PF bonds formed at 110°C and either cooled to 34°C before being pulled or tested hot are shown as Figure 6.

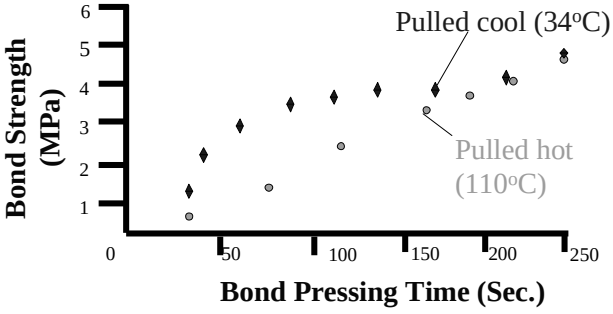


Figure 6. The effect of cooling on partially cured PF-to-wood bond strength for bonds pressed at 110°C.

Bond pressing times used in Figure 6 are defined as the lapse of time from

when the pressing blocks close on the bond to when the blocks are retracted. Forced cooling was initiated within one second of press opening and the polymerization rate thereby all but halted within three seconds. It is evident that cooling of partially cured bonds greatly increased their shear strength and that the effect declines as cure progresses. For example, after 55 seconds of pressing at 110°C, the differential of bond strength between 34°C and 110°C is 1.4MPa; this corresponds to a cooling-induced strength increase of 142%. However, after 220 seconds of isothermal pressing at 110°C, the effect of cooling had almost entirely ceased. It is hypothesized that cooling effects cease once the T_g of the adhesive climbs to the bond forming temperature.

The above and more extensive supporting data imply that the strength of partially cured thermosetting bonds may be increased by lowering their temperature. With the advent of gas injection presses, a diversity of new pressing technologies may enable cooling prior to press opening (gas release affecting an adiabatic cooling effect), and thus reductions in pressing time.

Chemical injection into PF bonds as they are being pressed.

Work of Pizzi and his co-workers suggests that resole PF resins are surprisingly stable at high pH. It was therefore hypothesized that fibres pre-dosed with PF may be exposed to gaseous ammonia for rapid room temperature softening without stimulation of resin cure, and that vapour-phase methyl formate (an ester) may be subsequently injected to catalyse the resin. Before adopting this strategy in a sealed pressing system to rapidly form new composites without the need for costly heating, ABES was used to evaluate the effect of NH_3 and methyl formate on wood-PF resin bond strength development. This was done in order to verify the feasibility of employing the approach in the sealed pressing system.

Figure 7 represents the basic principle of such bond formation with chemical injection, together with a photo of one of the pressing heads.

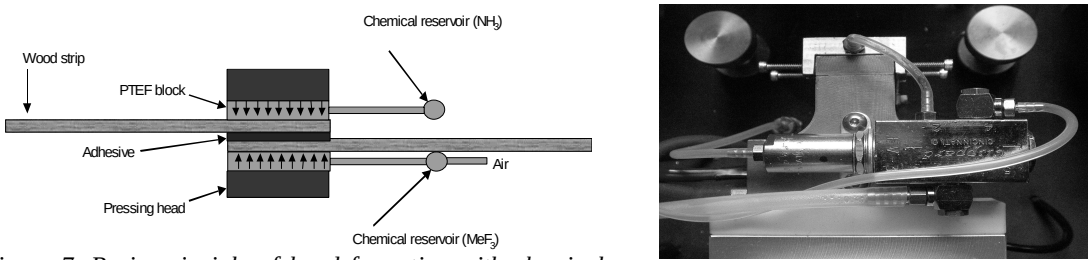


Figure 7. Basic principle of bond formation with chemical or steam injection (above) together with one of the two heads (right).

The effect of a range of chemical injection sequences on bond strength development has been explored, and a representative set of data are shown as Figure 8. Evidently, the addition of ammonia did not detrimentally stimulate resin cure, but the subsequent addition of methyl formate did lead to rapid strength development. The results of the ABES testing provided justification for trials with resinated fibre mats in the sealed pressing system that was subsequently designed and employed.

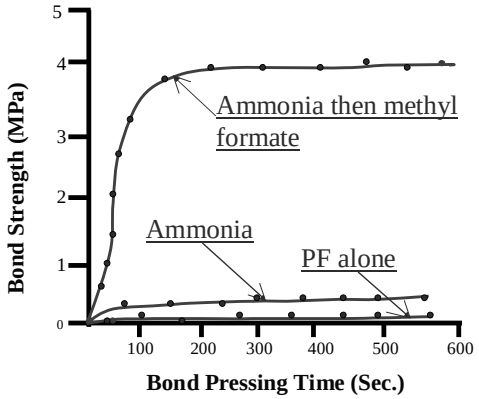


Figure 8. Strength development data with three combinations of chemical treatment.

Moisture and spread-rate effects on pMDI adhesion

The computer controlled fluid injection system enables steam as well as reactant fluids to be applied to bonds at precisely selected stages during bond pressing. This system enables some control of moisture conditions under which bonds are cured to be affected. It was used to explore the moisture dependency of pMDI adhesives. A plot is shown as Figure 9. This is for a spread rate of 10 g/m^2 and bonds pressed at a single temperature of 110^{o}C. Clearly, the kinetics of pMDI adhesives is highly effected by the presence of moisture and such information may be used to aid in optimizing adhesion within industrial panels as pressing progresses – where both temperature and moisture conditions vary in space and time.

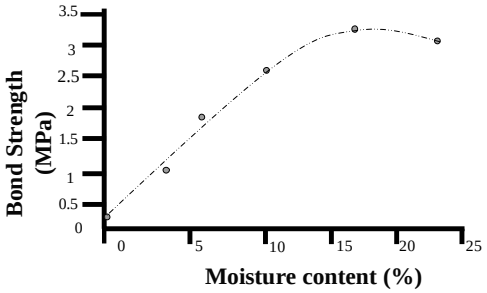


Figure 9. A plot of the effect of moisture content on isothermal strength development of a pMDI adhesive.

The effect of spread rate on pMDI adhesives for wood bonding is also a critical factor both because of the cost of the adhesive but also because the application of too much adhesive actually is a detriment to bonding efficiency. The precision micro-spray system (an ABES accessory) enables spread rate on micro-bonding surfaces to be precisely metered over a wide range (from 2 g/m^2 to saturation.) Some control of droplet size and its consistency is also achievable. A representative set of data showing the effect of spread rate on isothermal strength development is shown as Figure10.

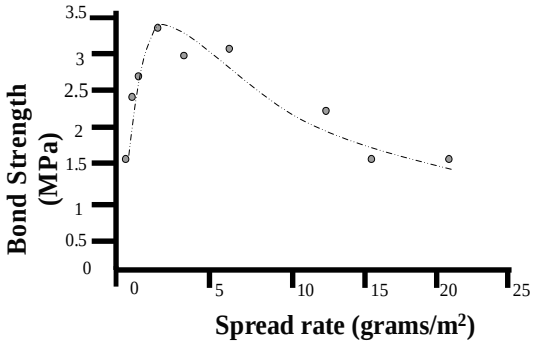


Figure 10. The effect of spread rate on pMDI bond strength.

Thermal damage to UF adhesives

It is widely acknowledged that the strength of UF bonded panels may be reduced by prolonged exposure to heat after pressing. ABES may be used to quantify the susceptibility of bonds to heat – both after full cure, but also during the curing process itself. This information is valuable in optimizing pressing cycles for panels and selecting adhesive formulations for surface layers of panels. A family of ABES data for bonds formed at temperatures ranging between 95^{o}C and 140^{o}C is shown as Figure 11. Near-linear isothermal strength development is evident for the early stages of each plot. Strength development rates must, however, inevitably decline and maxima reached. Subsequent decline in strength is clearly evident and its rate is greatest at high temperatures – thus implying thermal damage. Indeed, the peak strength of bonds pressed at lower temperatures exceeds those at high, possibly due to thermal damage that occurs in the latter even before the peak value is reached. Regressed rates of both isothermal strength development and decline due to thermal damage are shown as Figure 11 (right).

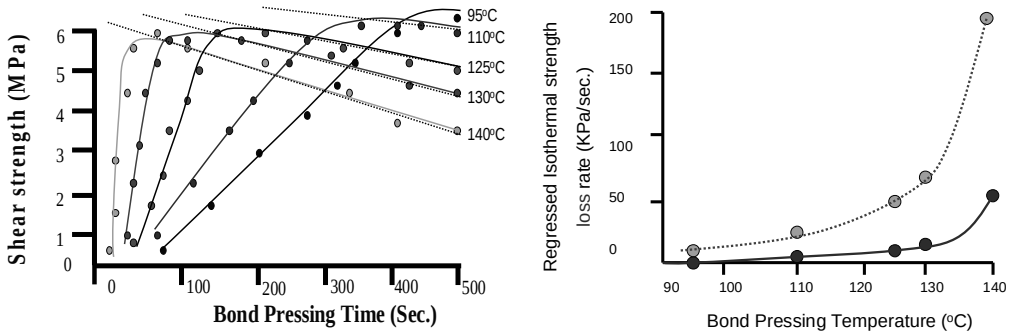


Figure 11. Isothermal strength development plots for UF adhesive, showing thermal damage (declining strength) at high temperatures (left). Regressed rates (right) of development (upper blue curve) and decline (lower red curve).

It seems likely that bonds formed rapidly at the surfaces in the early stages of panel pressing may be thermally damaged as such temperatures are maintained during the cycle. The decline in peak strength for bonds pressed at high temperature highlights this dilemma.

CONCLUSION

It has been shown that the Automated Bonding Evaluation System enables the strength development characteristics of adhesives and substrate combinations to be explored as a function of a wide range of parameters. The technique allows the compatibility of adhesives for industrial manufacturing processes to be evaluated and refined. In this way, the system can help adhesives manufacturers to tailor existing and new products to specific applications in the formation of diverse composite and laminated products. Those who use adhesives in their product manufacturing operations may use the technique to help them select the best type of adhesive to suite their manufacturing process; it may also aid them in adjusting their process to get the most from the adhesive that they select.

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