AN ABSTRACT OF THE THESIS OF

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Title: <u>Bonding Kinetics of Thermosetting Adhesive Systems Used in</u>

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Abstract approved _____

                     Dr. Philip E. Humphrey

Bonding kinetics of thermosetting adhesives plays an important role within wood based composites during hot pressing, and in determining appropriate processing schedules for the manufacture of composites. A dynamic method has been developed to offer a direct means for investigating physical transformations that occur during bond formation, and the influence that temperature and moisture content together have on this process. Environments for each test are maintained constant and uniform throughout the cross-section of the wood-adhesive combination by injecting selected atmospheres of the appropriate temperature and relative humidity into the sealed pressing system. Desired bond forming conditions are therefore maintained near constant within the system. Many bonds have been formed under a range of steady-state temperatures and moisture contents and immediately tested in tensile mode after a range of forming times. New instrumentation has been developed which is enabling the development of bond strength to be analyzed fundamentally and quantitatively while varying these parameters.

Because the factors involved in hot pressing wood based composites are so interactive, this numerical data linking temperature and moisture content to strength development rates during the formation of test bonds is necessary. This is in order to understand how the conditions that occur in composites during pressing effect bonding. Such basic information can then usefully be used in computer simulation algorithms to model what goes on in the composite. These models may then be used as tools both for the optimization of existing processes and for the development of new materials and generic products.

Bonding Kinetics of Thermosetting Adhesive Systems

Used in Composites

by

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ACKNOWLEDGMENT

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CHAPTER I

INTRODUCTION

The bonding kinetics of thermosetting adhesives plays an important role within wood based composites during hot pressing. Gradients of temperature, moisture content and vapor pressure develop in the three dimensions of the composite during pressing. The continuous variation of these variables throughout the panel during hot pressing effects the process of adhesion and the development of bond strength. Bonding in turn effects the properties of the final products, and also the required hot-pressing time and energy consumption.

Because the factors involved in hot pressing are so interactive, we have to carefully design our experiments and initially preclude some factors so that we can achieve valid and useful fundamental analysis. Numerical data linking temperature and moisture content to strength development rates during the formation of test bonds is necessary in order to understand how the conditions that occur in the panel during pressing effect bonding. Such basic information can then usefully be used in computer simulation algorithms to model what goes on in the composite. These models may then be used as tools both for the optimization of existing processes and for the development of new materials and generic products.

The development of new composite materials will increasingly depend upon effectively coordinating fundamental processes operative during

hot pressing. These processes include the following:

---- heat and moisture flow with phase change

---- adhesive polymerization

---- physical compaction

While various analytical techniques have provided information on chemical changes during adhesive cure, dynamic mechanical methods offer a direct means for measuring physical transformation that occur during cure.

Objectives of the research:

The principle objective of the present research is therefore to provide numerical (quantitative) understanding of the influence of moisture and temperature on the bonding kinetics of thermosetting adhesive systems used in composite manufacture.

To achieve this goal, the following constituent objectives have been established for the present project:

1. The design and development of new equipment and techniques for analysis of the adhesion kinetics of thermosetting adhesives.

2. The provision of numerical data for later incorporation in a global simulation of physical and thermodynamic processes operative within wood-based composites during hot-pressing.

3. The provision of better fundamental understanding of the nature of bonding system behavior.

Many research workers have studied the hot pressing of composites. Most have used empirical methods, which provide good experimental data to support general descriptions of the process. They do not, however, solve the problem numerically, and do not provide the necessary fundamental understanding. These may be called methods of macro-analysis. A limited number of researchers have worked theoretically and some formulations or functions in mathematics, thermodynamics, chemistry and physics have been developed. Very few of these have been supported or verified experimentally. These may be called methods of pure analysis. New approaches which improve on the above two methods and connect them together could prove very useful. The complexity of wood's structure and properties makes the use of rigorous techniques difficult. What is proposed here is an approach which will provide data upon which predictions of bond strength development during hot-pressing may be based.

According to this principle, a dynamic method has been developed to offer a direct means for investigating physical transformations that occur during bond formation, and the influence that moisture and temperature together have on this process. For this purpose, sample bonds are formed and tested under a range of accurately controlled steady-state conditions of temperature and moisture content. The adhesion kinetic characteristics may then be studied. A specially designed device capable both of compression (bond forming) and tension (bond testing) has been used for this purpose. This consists of a miniature hot press system which is mounted on the servo-hydraulic testing machine (MTS). Environments for each test are maintained constant and uniform throughout the cross-section of the wood-adhesive

combination by injecting selected atmospheres of the appropriate temperature and relative humidity into the sealed pressing system. Desired bond forming conditions are therefore maintained near constant within the system.

Many bonds have been formed under a range of steady-state temperatures and moisture contents and immediately tested in tensile mode after a range of forming times. Curves of bond strength versus pressing time are derived for each of the selected combinations of temperature and moisture content. The relationship between rate of bond strength development and temperature, moisture content and pressing time may then be quantified.

The data generated from these experiments will, in future research, be used in a global simulation of physical and thermodynamic processes operative within composites during hot pressing. Rheological models for wood based composites during pressing (densification and stress relaxation) are presently being developed, while those for heat and moisture transfer are complete.

CHAPTER II

DISCUSSION OF SELECTED LITERATURE

2.1. Introduction: The need to study bonding kinetics

The study of bonding kinetics in wood composites here concerns the rate of bond strength development during hot pressing, and the effects that temperature and moisture content have on this. This literature review will be concerned with these aspects. The interaction of adhesion with other aspects of composite manufacture will, however, be discussed in section 2.1.1.. Sections to follow this will consider adhesion firstly from the material standpoint [structure (2.2) and adhesive (2.3)] and secondly in terms of processing (2.4).

During the development of bond strength, thermosetting resins cure by transformation from a relatively low molecular-weight liquid or powder to a highly cross-linked and usually amorphous solid. There are a number of methods used to indicate the quality of the adhesive cure and the effectiveness of the wood-adhesive interaction once the bond has been formed. Examples of such work are Chow (1969); Strickler (1959); Kollmann (1975). Little is known about the changes in bond strength occurring in the glueline during cure, and the morphological properties of the final cross-linked polymer. What really happens during bond formation, and how bond strength development is influenced by temperature, moisture, pressing pressure, pressing time are still not very clear.

Numerical approaches and simulation models have been used to

describe thermodynamic aspects of the composite system (Humphrey and Bolton,1979,1982,1985.). The three basic interrelated groups of processes that act during hot pressing to affect the formation of an integral composite with specific properties were identified in Chapter I. The basic interactive pathways between these processes were represented schematically by Humphrey and Bolton (1985) see Figure 2-1.

Rigorous numerical analysis of the system is of importance to optimize process conditions during the formation of wood-based composites. The study of bonding kinetics is an important aspect of this analysis.

The development of adhesive bond strength during hot-pressing is dependent on many factors. These may be divided into two broad areas:

1. material properties
2. processing conditions

These factors interact during hot-pressing and lead to complex influences on bond development. A review of all literature related to adhesion of wood would not be useful here; only information which is relevant to our research concerning the behaviour of composites during pressing will be considered.
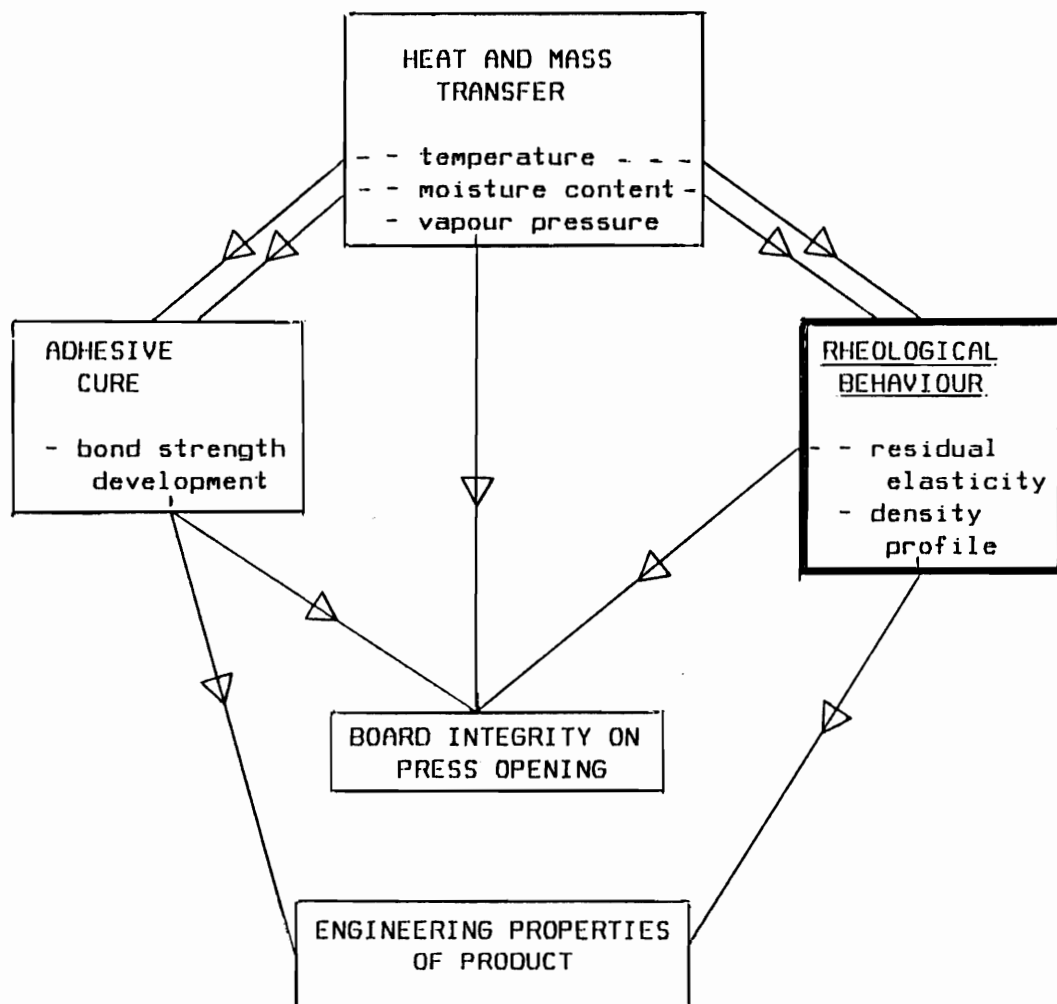
Figure 2-1. The relationships among processes operative
within composites during hot pressing (from
Humphrey and Bolton,1985)

2.2. Thermodynamic conditions that occur within wood-based
      composites during hot pressing

The distributions of temperature and moisture within panels change
continuously during hot pressing. A logical point at which to begin
analysis of the processes that lead to these variations is with solid
wood. A number of theories have been developed to better understand the
mechanisms of heat and mass (moisture) movement in solid wood, and
these have principally been in relation to the drying process. Examples
of such investigations are numerous and include those reported by Skaar
(1972); Siau (1984); and Rosen (1981). Rigorous numerical description
which accounts fundamentally for contributory mechanisms does, however,
remain illusive. These include unsteady-state interactions among the
following:

    a. conduction

    b. bound water diffusion within and between cell walls

    c. phase change

    d. vapor convection

    e. liquid water movement and the effects of drying induced
       stresses.

The combination of thermodynamic processes operative within wood-
based composites during pressing are similar in their fundamental
nature to those in solid wood during drying, but their relative
importance differ significantly. The steepness of gradients and the
resultant hostility of the environment within panels make rigorous
understanding of the processes all the more important.

Heat may be transferred in porous materials in three ways:

conduction, convection and radiation. Only heat conduction and vapor convection (following phase change) are thought to play an important role in the pressing of composites. Radiation may contribute slightly to heat flow across voids in the porous material, but its effect is considered insignificant (Strickler,1959; Humphrey,1982). During hot pressing, heat transfer will be in three directions and be a function of time. Fourier's law may be used to describe unsteady-state conductive heat transfer:

$$\partial T/\partial t = a^2 \ (\partial^2 T/\partial x^2 + \partial^2 T/\partial y^2 + \partial^2 T/\partial z^2) \qquad (2.1)$$

and $a = \lambda/c\rho$

Here, T = temperature
x,y,z = three mutually perpendicular spacial axes
t = time
T / x = gradient of temperature in x direction
T / t = rate of temperature change
a = thermal diffusivity
c = specific heat of material
ρ = density of material
λ = thermal conductivity coefficient

The rate of conductive heat transfer clearly depends on the magnitude of the temperature gradient and the thermal conductivity coefficient of the natural. This coefficient is dependant on a number of material properties. Primary among these are density, moisture content and the structure of the material.

A coordinate system used to identify directions relative to the panel while in the hot pressing is shown in Figure 2-2. During pressing of wood-based composites, heat is conducted from the press platens to the center of the board until the temperature at the center of the

board approaches that of the platens. On the other hand, when the temperature of the board rises, differences between the board and outside temperature increase and some heat is transferred from the edge of the board to the atmosphere. Heat is, therefore, also transferred horizontally from the center to the edge of the board (in x and z directions of Figure 2-2).
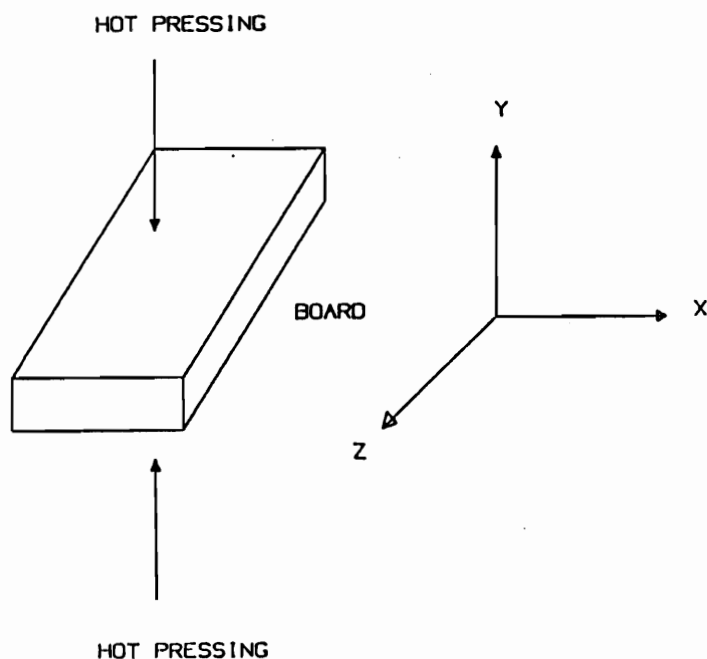
Figure 2-2. A coordinate system relative to the panel in the hot press

During the early stages of research, a number of workers noted that overall furnish moisture content, and moisture content distribution effect such physical properties of composites as layer density, modulae of rupture and elasticity, internal bond strength and dimensional stability (Strickler,1959; Chow,1969; Kollmann et al.,1975). These factors also effect the penetration rate of platen heat to the board

center, and therefore also the rate of temperature rise there. This, in turn, determines resin polymerization rates. The role that moisture plays in heat transfer during hot pressing is clearly extremely important. Phase change and subsequent convection of water vapor contributes more than conduction to the rapid transfer of heat energy into the board center. This has been asserted by a number of workers (Koch,1986; Lu,1981) and confirmed by Humphrey (1982, 1987).

The rate at which heat moves through the board from the surface is clearly a function of moisture content, the energy associated with the change of phase of adsorbed water into water vapor, and subsequent diffusion and re-adsorption of the vapor. This diffusion of water vapor leads to the re-distribution of adsorbed water within the panel. The development of gradients of moisture content in the three dimensions of the panel results. Moisture will also be lost from the edges of the panel where only the partial pressure of the water vapor in the surrounding atmosphere prevails. Escape of vapor from the surfaces of the panel in the press will clearly be prevented by the presence of the platens.

Moisture movement from one location in the material to another is therefore dependent on localised gradients of temperature and moisture content together with the hygroscopicity and permeability of the material. Moisture movement through porous materials (in one direction) may generally be described by an expression of the following form:

$$V = -a' \rho \ (dW/dx + \delta \ dT/dx) \qquad (2.2)$$

$$\delta = -\Delta W/\Delta T$$

Where: T   = temperature
        W   = moisture content
        x   = direction of heat and moisture transfer
        dW/dx = gradient of moisture content
        dT/dx = gradient of temperature
        δ = coefficient of heat and moisture transfer (a combined
                term here for simplicity which indicated the
                convection, bound water diffusion, capillary flow).
        V   = quantity of moisture flow
        ρ = density of material
        a'   = moisture diffusivity

The natural laws governing vapor movement may not be applied
directly to composites because most of the moisture in the board does
not reside there in the vapor state. Furthermore, unless the moisture
content exceeds the fiber saturation point, water is adsorbed within
the structure. If the moisture content does exceed fiber saturation
point, the pressure of water vapor in the voids of the material is the
same as that which normally prevails in the vicinity of liquid water at
the prevailing temperature (liang,1982).

Free water evaporates from liquid surfaces at temperatures above
freezing whenever the relative humidity of the ambient atmosphere is
less than 100 percent. Water in wood at less than fiber saturation
(about 30% moisture content) is hydrogen bonded within the materials
structure. As the moisture content of wood decreases, the attraction
between the wood and the adsorbed water molecules increases
(Skaar,1972) and so does the energy needed to remove them.

The anisotropic porous, viscoelastic and hygroscopic nature of the
composite clearly results in a unique complexity compared with the
processing of many other engineering materials. Thermodynamic behavior
of the system has, however, recently been tackled by Humphrey et al
(1982,1985,1987). In this work attempts have been made to simulate the

system fundamentally using numerical methods of integration. The
physical dimensions of the panel while in the press are divided into
small increments of length. Simulation progresses by considering
interactions between these defined regions for small time increments.
If the time increments are sufficiently small, steady-state conditions
of temperature and vapor pressure may be approximated, and simple
equations may be used to calculate flow of energy and vapor during each
increment. Updating the status of all regions at the end of each time
increment enables simulation to proceed. The updating procedure
involves the calculation of new equilibrium conditions of temperature,
adsorbed moisture content, vapor pressure and relative humidity for
each region.

What follow (Figures 2-3 through 2-5) are a set of typical results
produced by the simulation program. Figure 2-3 shows the variation with
time of the four thermodynamic variables output by the program. Each
curve corresponds to a different position within a vertical cross
section of the panel. These positions are identified by code numbers
varying from $Z = 1$ (core layer) to $Z = 10$ (surface). This cross-section
lies at the centre of the panel's plane.

Figures 2-4 and 2-5 show the variations of the four variables at
different positions within the vertical cross-section, and horizontal
position within the core layer respectively. Curves are presented for
seven different stages during a simulated pressing time of 600 seconds.

The simulation model accounts for conduction, phase change and
convection. It produces three dimensional distributions of temperature,
absorbed moisture content, and within void vapor pressure and relative
humidity. Predicted variations in each of these variables that occur

within the panel have been presented here because they reflect the thermodynamic conditions under which the adhesive bonds must form, and this is of primary concern in the present research.
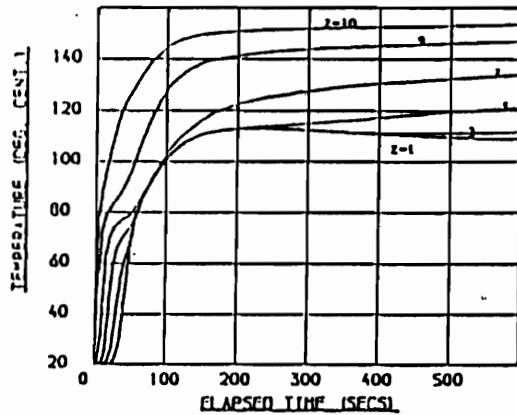
Central temperature vs. time   Central pressure vs. time
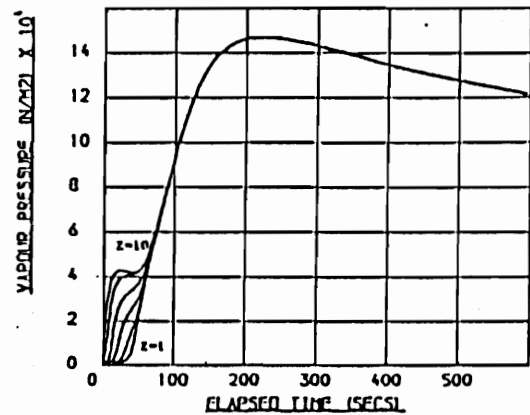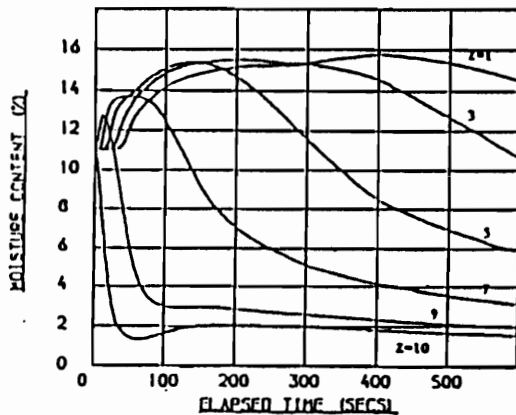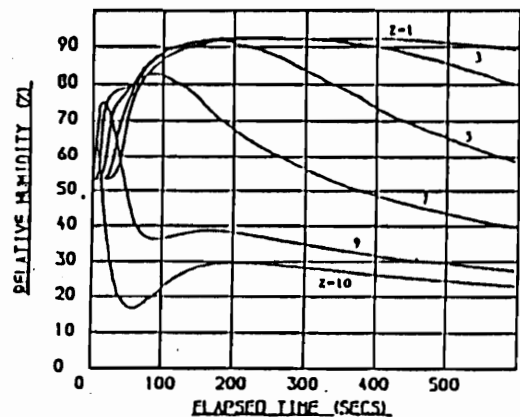
Central mc vs. time   Central RH vs. time

Figure 2-3. Predicted variations in temperature, vapor pressure, moisture content and relative humidity that occur at various cross-section positions within the panel during hot pressing (from Humphrey,1982)
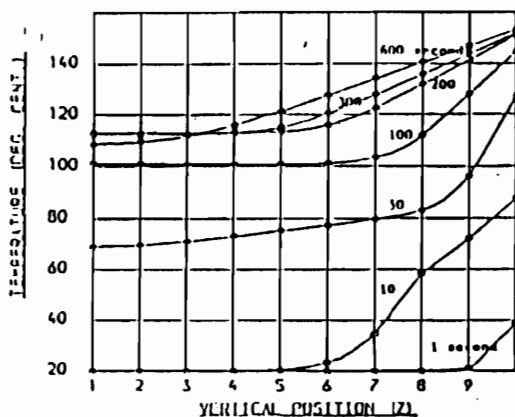
Temperature vs. vertical pos-
ition (Z) at the central axis
(where R = 2)
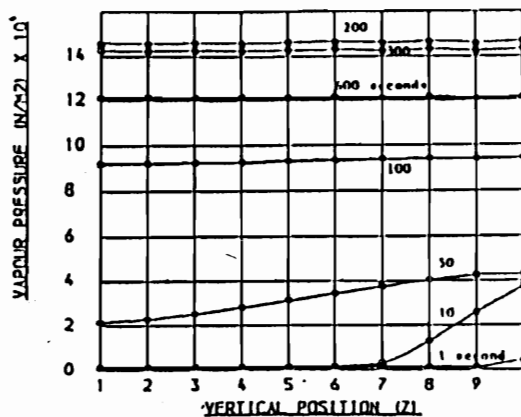
Pressure vs. vertical position
(Z) at the central axis where
R = 2)
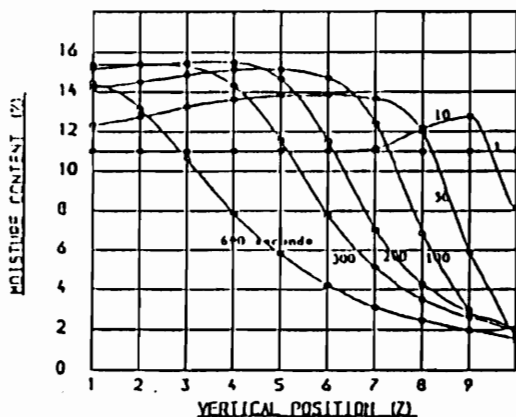
Moisture content vs. vertical
position (Z) at the central
axis (where R = 2)
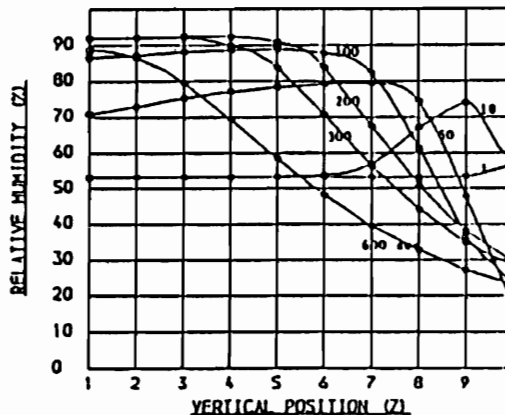
RH vs. vertical position (Z)
at the central axis (where
R = 2)

Figure 2-4. Predicted variations of temperature, vapor pressure,
moisture content and relative humidity with vertical
position at the horizontal centre of the panel (from
Humphrey, 1982)
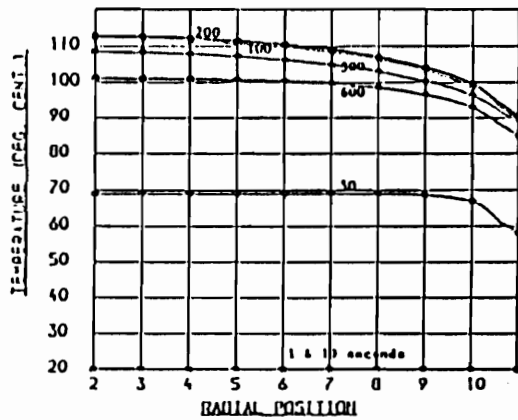
Temperature vs. radial position
(R) at the central plane (where
Z = 1)
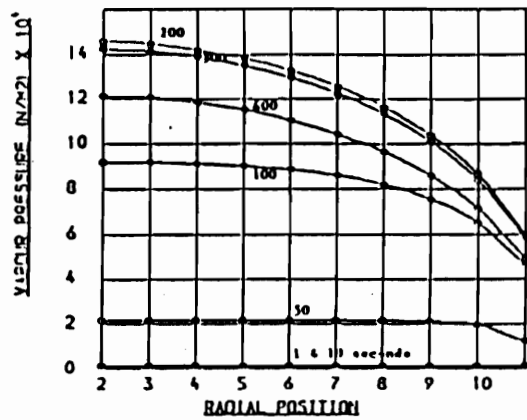
Pressure vs. radial position (R)
at the central plane (where Z=1)
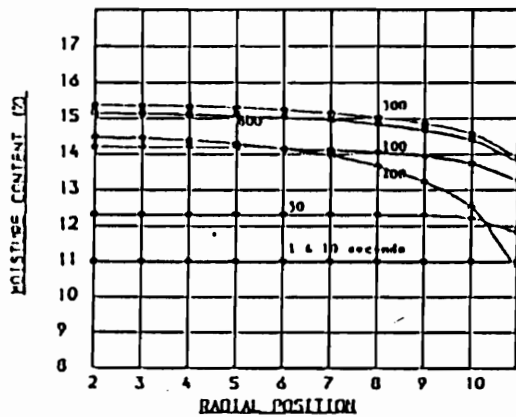
Moisture content vs. radial pos-
ition (R) at the central plane
(where Z = 1)
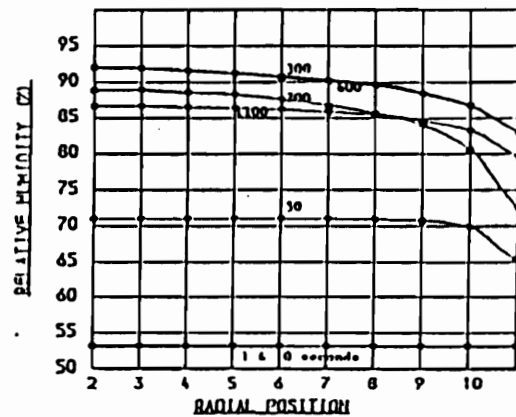
RH vs. radial position (R)
at the central plane (where
Z = 1)

Figure 2-5. Predicted variations of temperature, vapor pressure,
moisture content and relative humidity with horizontal
position across the board at the core layer. (from
Humphrey, 1982)

2.3. The mechanism of adhesion and bond failure in porous
materials

Before considering bonding and failure in wood based composite
materials specifically and how they may be measured, a general
discussion of the mechanisms involved in these processes will be
included.

2.3.1. Mechanisms of bond formation

The forces that cause an adhesive to wet, spread, and attach to the
surface of wood have been ascribed to chemical bonds, to mechanical
entanglement, to physical and chemical adsorption due to polar groups,
to electrostatic forces of attraction inherent in all matter, and to
combinations on all these effect (DeLolis, 1968; Gent and Hamed,1981).
Marra (1981) likened the adhesive bond to a chain with nine links. Each
of the nine links can be associated with specific actions or reactions
that affect both bond formation and bond performance. see Figure 2-6.
In Marra's model, links 8 and 9 represent not only the strength of the
wood but also its physical, chemical, and anatomical properties. As
these two wood links change in dimension, their influence on bond
formation and bond performance also changes. Links 6 and 7 represented
the nature of the subsurface of the bond, while links 4 and 5
represented the actual surface where adhesion forces of wood and
adhesive are supposed to engage one another.
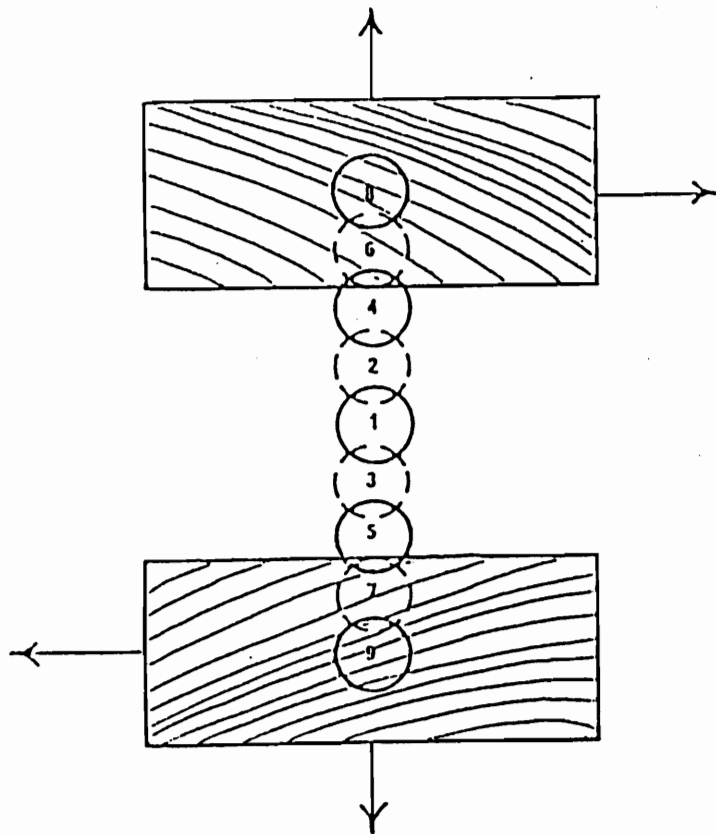
Link 1.   The adhesive film.

Links 2 and 3. Intra-adhesive boundary layer, strongly
               influenced by the adherend.

Links 4 and 5. Adhesive-adherend interface, site of adhesion
               forces.

links 6 and 7. Adherend subsurface, partially fractured in
               preparing the surface.

links 8 and 9. Adherend proper.

Figure 2-6. Nine links of an adhesive bond (according
            to Marra,1981)

Links 2 and 3, although part of the adhesive layer, require special attention because they may be only a few molecules thick and unidentifiable; this is the part of the adhesive layer that could be most strongly influenced by the chemical and physical properties of the wood. The center link directly affects performance; it is either stronger than or weaker than the wood. In the former case, it is not easily visible in a destructively tested joint since both ruptured surfaces will show only wood. In the latter case, fracture surfaces will be covered with adhesive on both surfaces and, if accompanied with low strength, indicates incomplete solidification of the adhesive. Bond failure may, then, result from failure of any link in this hypothetical chain.

Adhesive forces hold two materials together at their surfaces. Cohesive forces hold adjacent molecules of a single material together. Both adhesive and cohesive forces are primarily the result of unlike charge attractions between molecules (Collett,1972). Collett (1972) also pointed out that if one were to list theories or concepts of adhesion, it would likely compose of the following:

a. theories attributing adhesion to forces holding atoms and molecules together

b. theories based on surface energetics and phase boundary phenomena

c. theories based on thermodynamics of wetting and adsorption

d. weak boundary-layer theories

e. theories based on surface roughness

f. theories of polar-non-polar adhesion

It is not our purpose to discuss these theories in detail, but the nature of atomic and molecular forces will be reviewed a little more here.

When considering the chemical bond in adhesion, the type of forces involved becomes important. Beginning with the molecule, there are the intramolecular forces of attraction and repulsion, which are related to electron charge and spin. These intramolecular forces actually determine the structure of the molecule, as all movement of electrons will be toward the greatest balance of the attractive and repulsive forces and the lowest possible energy state (Pimental and Spratly,1969; Rice,1981).

The covalent bond is a very important bond type in wood adhesives. The covalent bonds of certain molecules have a property called polarity. This polarity of bonds can lead to polarity of molecules, and thus can profoundly effect melting point, boiling point,and solubility (Gent and Hamed,1981).

The ionic bond, which involves the transfer of electrons, is as important in the wood adhesive as the covalent bond. There are two kinds of intermolecular forces: dipole-dipole interactions and van der Waals forces. Dipole-dipole interaction is the attraction of the positive end of one polar molecule for the negative end of another polar molecule. The most powerful kind of dipole-dipole interaction is the hydrogen bond (Mouison and Boyed, 1966). If molecules of non-ionic, non-polar compounds are to coalesce or solidify, there must also be forces that hold them together. Such attractions are called van der Waals forces.

A general theory must properly account for both the bonding process

and the un-bonding or fracture process. Subjects of scientific and
technological importance include the interplay of thermodynamics and
rheological considerations which control the molecular nature of the
interfacial bond.

Figure 2-7. presents a semiformal relation between surface
chemistry, rheology, engineering mechanics, and the adhesion phenomena
which was proposed by Kaelble (1971).
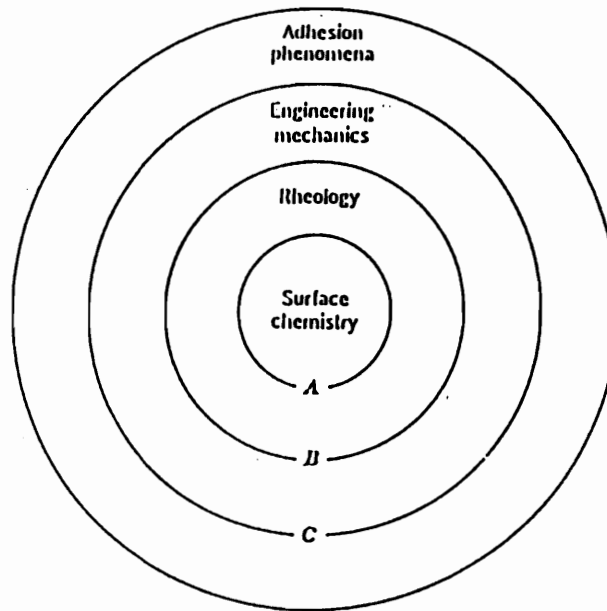
where: A = theory of interfaces

B = theory of fracture

C = model of mechanical phenomena

Figure 2-7. Correlation of several scientific disciplines which
contribute to the rationalization of adhesion phenomena
(from Kaelble,1971)

The case of cohesion or self-bonding of adhesive and adherent of identical chemistry and molecular structure provides an ideal basis for examining the rheological aspects of adsorption-interdiffusion processes. The only important restraints that limit cohesion-type bonding are of a rheological character. This is particularly true for low-energy substances such as high polymers which are chemically inert and do not tend to adsorb surface impurities physically. Aside from the scientific merit of understanding cohesion, it is obviously of great technological importance, since all plastic-forming processes, such as casting, molding, extrusion, and spreading are designed around criteria of cohesion bonding. The success of these manufacturing operations depends on the extent to which adsorption-interdiffusion bonding has been accomplished. Cohesive strength and toughness depend on the absence of imperfections in the internal structure.

Imperfections in cohesion may be classified into two categories:

a. Incomplete wetting and interfacial adsorption

b. Incomplete interdiffusion through the interface

Reduction and elimination of these interfacial imperfections can be directly associated with molecular processes of stress relaxation. Such effects are of critical importance in the bonding and failure mechanisms in wood based composites and paper. High compaction ratios and residual localised stress intensities in these products are critical in effecting their properties. These mechanisms are currently receiving attention in another research project (Humphrey and Bolton,1987).

Voyutskii differences the cohesion process of polymers from un-bonded to interface interdiffusion. Figure 2-8. indicates a two stage

bonding process involving firstly initial wetting and adsorption which forms a bonded interface that is structurally distinct from adjacent bulk phases. The second stage of cohesion bonding involves the interdiffusion of polymer segments and entire polymer molecules to re-establish the adjacent bulk phases. Only after the interdiffusion step has come to equilibrium does the cohesion interface of a polymer bond disappear.

SIMPLE LIQUID:

POLYMER:

UNBONDED   INTERFACE   INTERFACE
                  CONTACT   INTERDIFFUSION
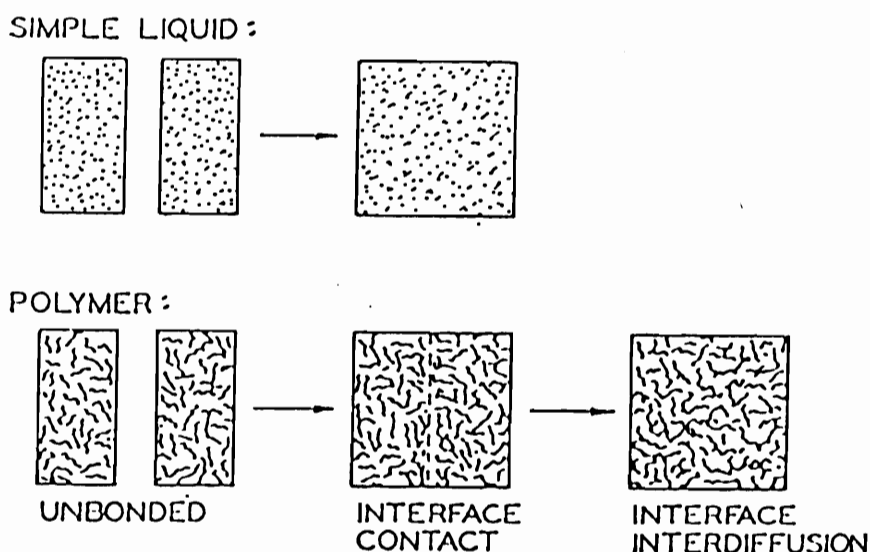
Figure 2-8. Stages of cohesion in simple liquids and polymers (from Kaelble,1971)

Several instances of non-continuous resin cure have been reported by researchers (Humphrey, 1977,1979,1982; Steiner and Warren, 1981,1987). These have mainly concerned urea formaldehyde (UF) resins.

A two-stage cure process appears to take place under varying heating conditions. During the initial cure stage, a limited bond strength increase is observed in the polymer. This is followed by a period of reduced and highly variable polymerization before rapid development of final, high bond strength in the second cure stage occurs. (see Figure 2-9). The cause of this discontinuous behaviour is not immediately apparent but it may well be partly linked to the types of behaviour described above.
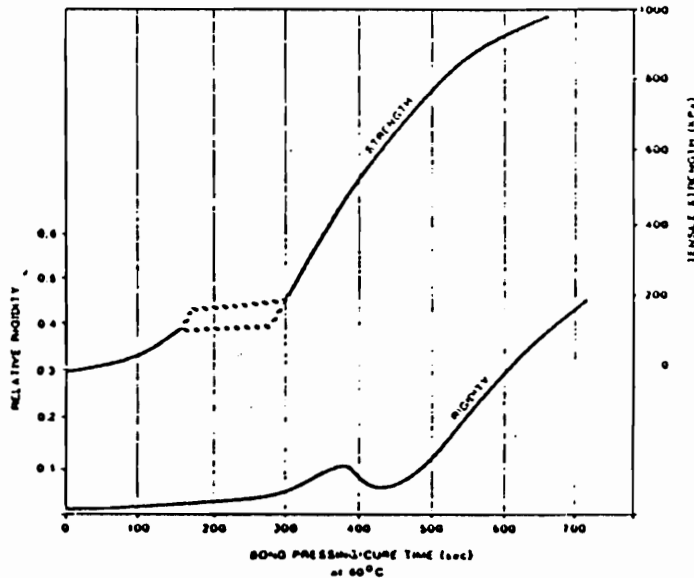
bond pressing cure time (sec.) at 60 °C

Figure 2-9. Comparison of strength development in UF bonded particleboard to a TBA cure rigidity profile of a UF adhesive (from Steiner and Warren,1987)

Jin (1986) observed that adhesive viscosity directly effects glue

spread, wettability, interfacial behaviour of the material and adhesive. Viscosity is clearly effected by temperature, the higher the temperature the lower the viscosity and also the lower the resin solids content the lower of viscosity. Wellons (1981) pointed out that the moisture in wood determines glueline moisture content and thus effects both the depth of adhesive penetration and the curing time of aqueous adhesives. In addition, excess moisture in wood will inhibit bonding of hot melt adhesives.

2.3.2. Mechanisms of bond failure

Kaelble (1971) pointed out that there are two groups of prominent factors that influence bond strength (see table 2-1).

The first group relates to characteristics which may be termed interfacial response, and the second relates to bulk properties of the adhesive joint and also to the conditions of destructive testing. Characteristics of destructive tests and measured joint strength may be related to the factors listed in Table 2-1. The successful use of destructive testing to examine a single one of the factors listed in Table 2-1 involves the careful and often ingenious design of the adhesive joint and test method.

A. Interfacial factors

      1. Dispersion-polar interactions

      2. Adherent wettability

      3. Adhesive-adherent cosolubility

      4. Surface adsorption layers

      5. Weak boundary layers

      6. Chemical bonding

      7. Special electrostatic effects

B. System factors

      1. Geometry of loading

      2. Joint design

      3. Adhesive rheology

      4. Adherent rheology

      5. Residual stresses

      6. Load induced stress concentrations

Table 2-1. Prominent factors influencing joint strength(from Kaelble,1971)

Common tests for adhesion may be roughly classified into five categories identified by Kaelble (1971) and shown in Figure 2-10. The test methods are schematically described by the action of the applied and reactive forces in the bond.

TEST	TYPE JOINT	Schematic of Joint & Applied Forces	Reaction of Bonding Forces
Simple Tension	Rigid — Rigid		
Cleavage	Rigid — Rigid		
Simple Shear	Rigid — Rigid / Rigid - Flexible / Flexible-Flexible		
Vertical Knife	Rigid - Flexible		
Stripback or Peel	Rigid - Flexible / Flexible-Flexible		

Figure 2-10. Tests for bond strength (from Kaelble,1971)

Tensile tests may produce shear and hydrostatic pressure effects as well as simple tension in the joint. Kyoken, et al, (1986) pointed out that the Circular-Bar Test (CBT) specimen results in fracture occurring in the interphase zone, defined by White (1977) to be the region where the adhesive penetrates into the wood. This geometry does not contain any square corners to perturb the tensile stress distribution. It will be seen later in the present work that this approach has been used in modified form by Humphrey and Bolton (1979) and will similarly be used here to study rates of bonding development. Clearly, considerable modification of the circular bar test is involved for this purpose and this will be described in detail later in the thesis.

Cleavage testing is a variant of simple tensile testing in that the external force is applied at the edge of the bond area. Equilibrium of

moments of force produce regions of compression as well as tension within the bond.

   Simple shear is shown to produce complex distributions of tension and compression as well as shear stresses in practical bonds. Figure 2-11. shows an ideal bonded lap joint under an applied tensile load (A), the resulting stress (shear) parallel to bond (B), an actual lap joint and load line (C), and shear stress plus tension or compression perpendicular to the bondline (normal stresses) (D).
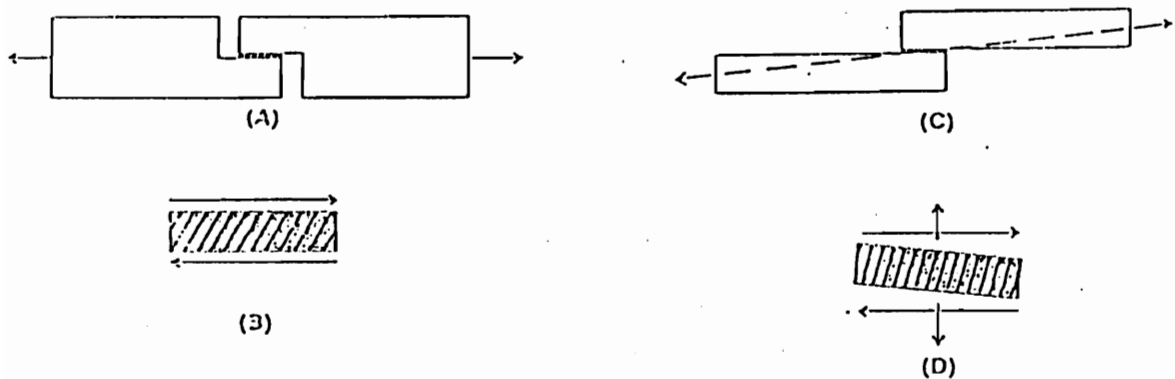
Figure 2-11. (A) Ideal lap shear specimen and (C) Actual lap shear
specimen (from River,1981)

   In the ideal case for measuring shear properties, the shear stress would be constant along the joint and no normal stress would exist in the adhesive. This condition, called pure shear, can not be very accurately achieved by conventional lap shear specimens because a variable mixture of normal and shear stresses occur in the joint. Apparent shear strength is actually a combination of shear and tension strength (River,1981). A shear test was used to study bond development

strength (River,1981). A shear test was used to study bond development characteristics of Phenolic adhesive systems used in plywood and laminate manufacture (Zavala,1985). A number of interesting phenomena were successfully observed in this work but still, inaccuracies in measured values resulted from the effects discussed above.

A disadvantageous property common to these first three test methods concerns the fact that the rate of deformation of the joint cannot be related directly to the rate of fracture. In other words, one cannot ordinarily control test conditions to achieve steady-state or constant rates of deformation and fracture within the joint. Analysis of fracture by a rate theory requires correlations to be established between the processes of deformation and fracture. Vertical knife test or the peel test is a simple means of producing a desired steady-state effect (a controlled boundary condition of deformation and fracture).

The limits of performance of adhesive joints formed with polymeric adhesives are ordinarily determined by the cohesive properties of the polymer. This criteria applies generally to well-bonded joints involving adherents of higher surface energy and cohesive energy density than the polymer adhesive interlayer. The subject of cohesive strength is of prime interest in determining the upper performance limits of adhesively bonded joints.

Mechanical stress analysis and fracture mechanics are subjects in the fields of engineering and materials science. A rheological experiment is a special form of mechanical test in which fracture is avoided by maintaining stress and strain at low amplitudes. The function of stress analysis is to correlate the macroscopic response in an adhesive joint to the microscopic response of an element of a joint.

2.4. The interaction of wood and thermosetting adhesives

The proceeding two sections have considered bonding and fracture mechanisms which are common to most adhesive situations. The present section concerns the special case of adhesion between natural fibers and particularly wood. This discussion will be divided into two parts: firstly from the point of view of the adherend (wood) and secondly from the point of view of the adhesive.

2.4.1. The effect of wood properties on bonding

The effects of wood properties on bond strength have been investigated by many workers and the following areas may be identified:

- wood structure and physical properties
- wood chemical properties
- wood sample surface energy and wettability
- wood properties effecting heat and mass transfer in the vicinity of the bond (permeability, hygroscopicity, conductivity, void volume etc.).
- orientation of wood fibers in the bond.
- moisture content and temperature of wood.

Unfortunately, there appear to be very few reports concerning how wood properties change during the pressing of bonds and how these effect bond formation. Some of the above factors will be briefly considered in turn.

a. Physical effects

It is clear that wood structure and the orientation of components within both solid wood and composites has an effect on the formation of continuous glue lines. Upon compression of composite mats in hot pressing, the amount of void space will be reduced, the mat will be densified. and surfaces will be brought together. Many anatomical characteristics of the interacting surfaces will then effect the nature of the bonding process that may follow. These are likely to vary in response to general characteristics associated with species and such factors as the anatomical differences between earlywood and latewood (Kollman,1975).

Latewood generally has superior mechanical properties, but it is contended that the higher density of this material results in more variation in swelling and shrinkage. This may lead to high stresses on the adhesive bond both during adhesive curing and in the final product. These stresses are clearly associated with movement of water within the material and resultant changes in moisture content values in the vicinity of the adhesive bond (Humphrey et al,1987). Investigations of Gaber (1937); Graf (1937/38), and Kuch (1943) suggest that tensile strength of adhesive bonds is maximized when they are formed at moisture contents between 8 and 10%. Strickler (1959) also pointed out that particleboard furnish moisture contents of 9% gave higher bond strengths in panels than those at 6% and 12% moisture content. The physical reasons for this maximum are not clear. It should also be remembered that localised moisture values vary greatly within such panels during pressing (see section 2.2), so initial mat values do not

provide any fundamental information upon which the processes may be characterized.

b. Surface conditions

Bonding surface characteristics directly influence resin distribution and subsequent strength of the bond. The earlywood exhibits good accessibility due mainly to the larger voids of the fiber lumen. This generates a larger active surface area for bonding (Mizumachi and Morita, 1975). Rough surfaces do not however, necessarily generate good bonds. It has been pointed out that adhesion between dry solid surfaces (autohesion) can be demonstrated under special circumstances. The split surface of a crystal of mica or glass freshly heat-treated (Baier et al,1968) probably presents the smoothest solid surfaces attainable. When referring to a smooth surface, only the surface of a liquid at rest is smooth on a molecular level. Such a surface might be said to have a roughness "r", equal to 1. All solid surfaces exhibit roughness values greater than 1; indeed, most of them do not approach anywhere near a smooth surface with respect to that presented by a liquid.

The roughness factor, "r", is often used to quantify the concept of roughness (Marian,1966, Collett,1972) and refers to how many times larger the true surface areas is than the geometric (apparent) surface area. Therefore, when roughness is great in comparison to the ideal, it is apparent that adhesion is enhanced under conditions of complete wetting. However, in the absence of complete wetting, roughness causes degradation of the adhesive joint. Incomplete wetting plays an

important role with stress buildup during solidification. Figure 2-12 shows wetting phenomena which are thought to occur when liquid is deposited on the wood surface.
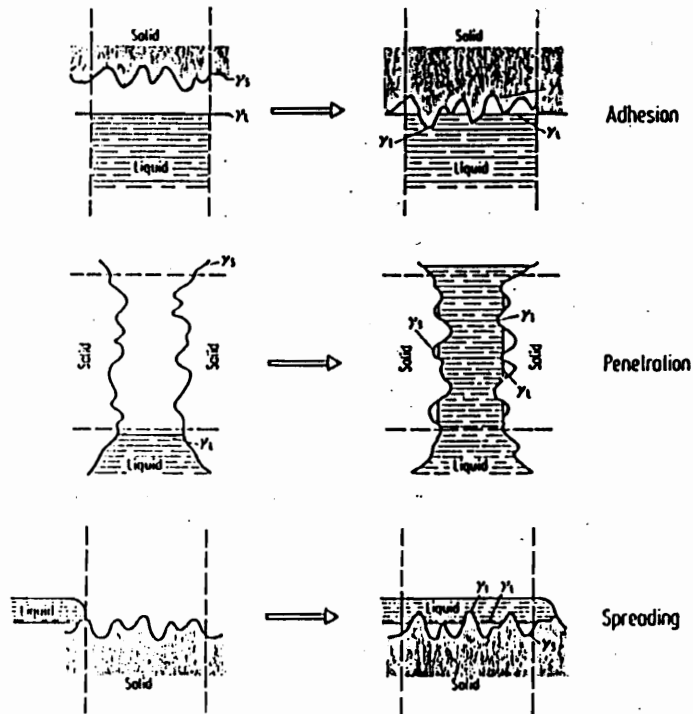
Figure 2-12. Wetting phenomena (from Patton,1970)

Gary (1961,1962) found that there was no consistent difference between wettability of the longitudinal, radial and tangential grain directions for wood specimens within a species. But on freshly sanded surfaces it was found that wettability decreased as a function of time and measurable changes occurred within an hour or so of sanding. Gary also pointed out that:

a. low surface tension leads to easy wetting but to inferior

adhesion.

b. high surface tensions lead to difficulties in applying the glue or finish.

c. the main benefit of sanding immediately before spreading is that it assists wetting.

d. woods with very different wetting characteristics can be made to yield very similar adhesion. (Collett,1972)

No standard surface was been established to evaluate bonding of wood, and no standard surface measuring method exits (Collett, 1972; Young, 1982, 1983.).

Wellons (1980) contends that phenolic type glues are less sensitive to the wettability of wood than UF resins. The effect of the roughness of wood is a characteristic that has still not been definitely established. The relationship between wettability and gluability of phenol adhesive remains disputed.

c. Chemical effects

The distribution of chemical components are non-uniform within wood and these distributions also vary between species. Of primary concern is the proportions and distributions of cellulose, hemicellulose, lignin and extractive. Cellulosic and hemicellulosic polymers are highly polar and have high surface energy values that attract and bond adhesives. Lignin may be considered to act like a concrete within the wood structure. It is not generally considered to be reactive with adhesives, but it may soften and flow under appropriate conditions of temperature and moisture content (above glass transition temperature)

and may then affect adhesion in composites.

The extractive include both polar and non-polar chemicals, and they may interfere with the wood-adhesive interface. They may form a barrier at the interface that may prevent wetting or cause mechanical weakness (Troughton and Chow,1971; Wellons,1980). It is also possible that certain extractive may effect polymerization of adhesive at the interface area. In addition, under high temperature conditions, the extractive may melt and migrate over the bonding surface causing it to be of reduced wettability.

2.4.2. The effect of adhesive properties on bonding

The study of adhesives used in wood-based composites is becoming increasingly important as work continues toward greater utilization of our total forest resources. The present quality of adhesively bonded wood composites must be improved in order to achieve bond quality that enables the full strength of wood to be harnessed, and leads to enhanced bond durability. These goals will primarily be reached through developing a chemically-anchored bond interface and resin systems that are more flexible and compatible in the cured state.

The most common adhesives presently used in the production of wood-based composites are phenol-formaldehyde (PF) and urea-formaldehyde (UF). Phenolic adhesives adhere well to polar substrate, have good high-temperature properties, resistance to burning, and have high strength. They are a relatively low cost means of achieving bonds which are durable in exterior situations. In recent years, they have not only dominated the U.S.A. plywood adhesives market, but also have been used

increasingly in the particleboard and waferboard industries. Phenolic may be formulated as water dispersions which have advantages in bonding wood where penetration into the cell structure is vital for the formation of permanent bonds. Here, we will briefly consider the structure and properties of phenol formaldehyde adhesives.

The main factors influencing adhesive properties related to bonding behavior (Rice,1975; Chow,1969) include:

a. percentage solid content in liquid adhesive

b. PH of adhesive

c. molar ratio of phenol to formaldehyde

d. catalyst type and reactivity

e. fillers, extenders

The mechanisms of polymerization and final structure of phenolic adhesives will be briefly outlined below.

Phenol-formaldehyde adhesive properties

The structure and properties of phenolic adhesives have received considerable attention by many researchers over a long period. These include for example Schneberger (1980), Subramainen (1981).

Phenolic are provided either as a one-component heat-curable liquid silution or powder, or as a liquid solution to which a catalyst must be added. The curing mechanism differs for these two types, heat curing and catalyst curing, as shown in the general formula in Figure 2-13. Phenolic are used in many areas, table 2-2 shows the material forms and application areas for phenolic adhesives.
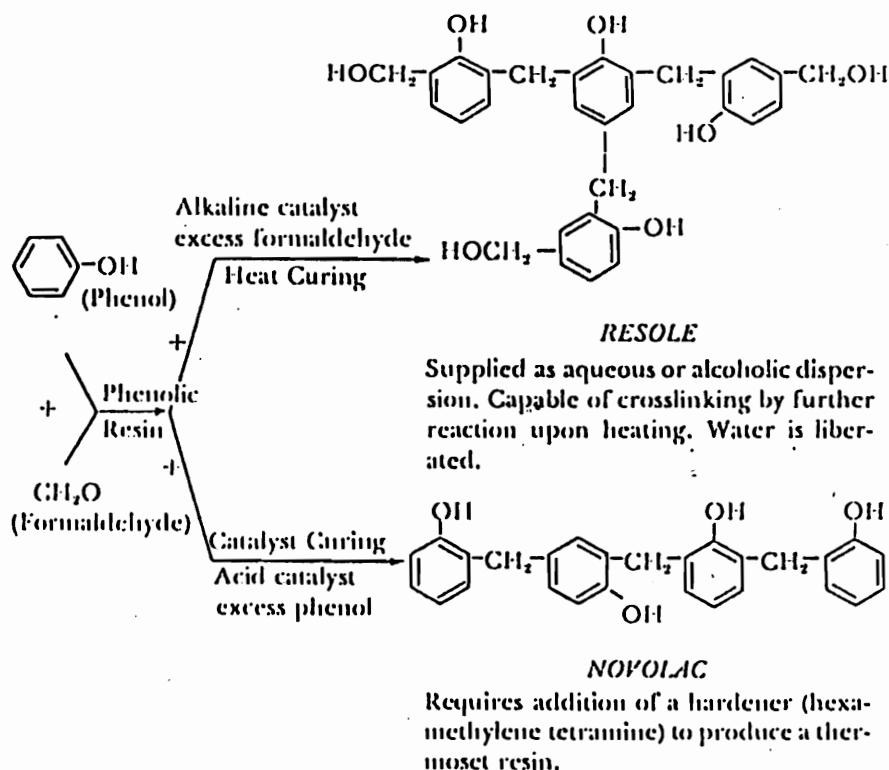
Figure 2-13. Curing mechanism of phenol-formaldehyde
adhesives (from Subramainen, 1981)

Material Forms and Application Areas for Phenolic Resins

			Phenolic resins			
Liquids	Solutions		Solids			
Neat	Aqueous	Organic	Lumps	Flakes	Pulverized	Dispersions
	Laminates Foams Foundry Coated abrasives Coatings Fiber bonding		Coatings Adhesives	Foundry	Fiber bonding Grinding wheels Wood bonding Friction	Friction Adhesives Coated Abrasive Coatings

Table 2-2. The application of phenolic adhesives (from Young and
Tancrede, 1981)

Resins are manufactured from phenol and a large number of substituted phenols through reaction with an aldehyde, primarily formaldehyde. The major chemical route to the most common reactant, phenol, is outlined in Figure 2-14.
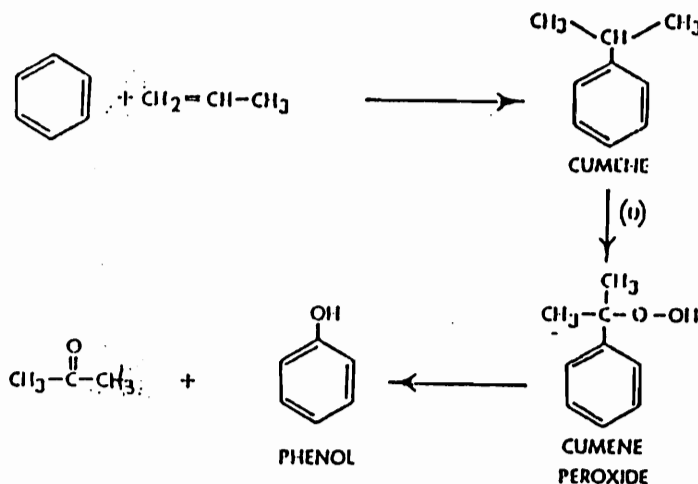
Figure 2-14. Novolac phenolic resin chemistry (from Scheberger, 1981)

Benzene is initially reacted with propylene to yield cumene. Cumene is then oxidized to cumene hydroperoxide which, in turn undergoes an acid-catalyzed rearrangement reaction to yield phenol and acetone.

The two basic chemical types of phenolic resins, resoles and novolacs may be differentiated by their phenol-to-formaldehyde ratio, the type of catalyst used in manufacture, and the chemical structure of the resulting resin. Table 2-3. shows these differeces.

Characteristic	Resols	Novolacs
Catalyst type	Alkaline	Acid
Mole ratio of CH_2O:phenol	> 1	< 1
Resin structure	High branched	More linear
Reactivity	Cures with heat	Requires both heat and hardener to cure

Table 2-3. Characteristics of resol versus novolac phenolic resin (from Scheberger, 1981)

These chemical differences are further illustrated in Figures 2-15 and 2-16.
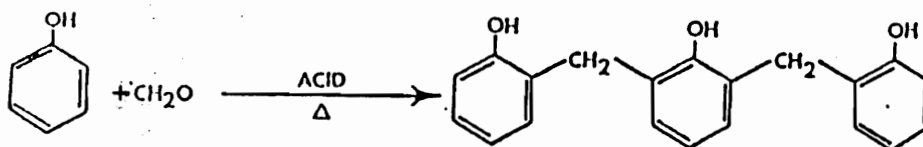
Figure 2-15. Novolac-phenolic-resin chemistry (from Scheberger,1981)
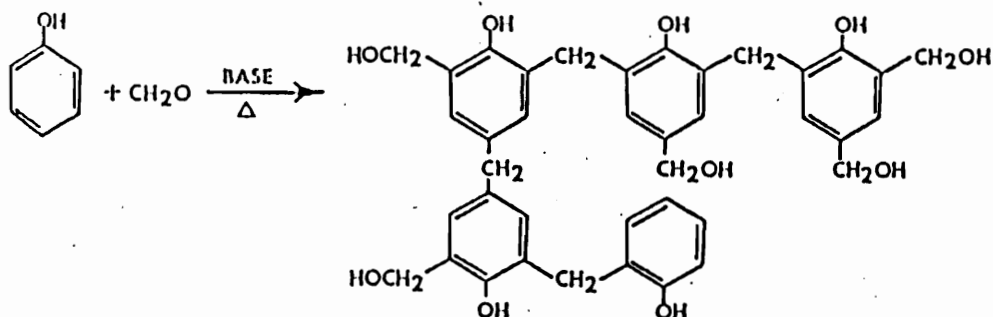
Figure 2-16. Resol-phenolic-resin chemistry (from
            Scheberger,1981)

A novolac resin is characterized by having no reactive methylol

groups but having un-substituted ortho and/or para reactive sites. At

these sites a hardener can react to yield a chain-extended and

ultimately, cross-linked polymeric system. A resole resin, on the other

hand, contains not only open reactive sites, but also reactive methylol

groups. The resoles require only heat to effect chain-extension and

cross-linking reactions. The cure of both types of resin is dependent

on temperature, catalyst type, hardening agents, concentration of

catalyst and/or hardening agents, and the type of phenol and aldehyde

used. The chemical reactions involved in the cure of phenolic resoles,

a substitution reaction by a methyl hydroxyl group, yield a methylene

ether linkage (Figures 2-17 and 2-18).
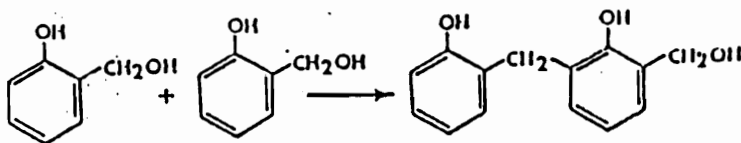
Figure 2-17. Chemical reaction of a resole phenolic to a methylene linkage (from Scheberger,1981)
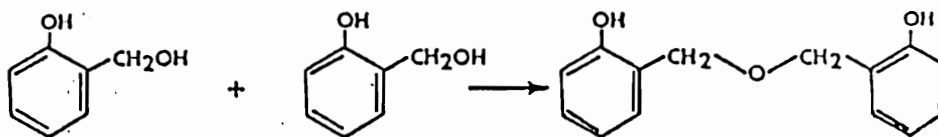
Figure 2-18. Chemical reaction of a resole phenolic to form a methylene ether linkage (from Scheberger,1981)

Chain-extension cross-linking reactions of the phenolic resole or novolac results in a fully cured system. Many factors contribute to the degree of this cure which, in turn, effects the performance of the ultimate product. The curing process involves three phases of reaction. The first phase results in the formation of low-molecular-weight oligomer and is designated as A-stage. This A-stage product is soluble in alcohol, acetone, or similar polar solvents and in solutions of

sodium hydroxide. The solid form will melt on being heated.

The _second phase_ involves the formation of an intermediate condensation product and is designated as B-stage. The B-stage is now insoluble in all solvents but may swell in acetone or similar chemicals. It will soften and can become somewhat thermoplastic-like on heating.

_Fully cured phase_s of the adhesive are termed C-stage. Here the phenolic is infusible and insoluble in most chemicals. The cured resin is now thermally stable, resistant to water and a good insulator to heat and electricity.

2.5. Measuring the rates at which bonds develop their strength

The rates at which adhesive test bonds develop strength under controlled conditions is of primary concern in the present project. However, little research in this area has been conducted. Most has been concerned with measuring the final properties of cured bonds. Here we have briefly reviewed some influences that temperature and moisture content have on the final strength of bonds. Information on the quantitative effects that temperature and moisture content have on the progressive development of bond strength is still, however, very limited. Some of the primary methods of inferring ultimate bond strength and characteristics will be outlined before going on to consider the direct method of measuring bonding rates.

2.5.1. Some indirect methods of predicting resin cure

It has, for example, long been standard practice to use shear strength and percentage of wood failure from block shear tests for assessing the quality of wood-adhesive bonds. This has been on bonds cured under pre-selected conditions of temperature and moisture content. Bergin (1964) used wood failure percentage as a glueability criterion but he also pointed out that strengths measured early in bond formation was not always a reliable indicator of ultimate bonding quality in his method. Therefore, the validity of using percentage of wood failure alone as an indicator of bond strength has been questioned. The effect of different wood characteristics, but not the temperature or moisture content, is said to be of prime importance in

affecting the results obtained using this method (Northcott,1955; Freeman,1959).

The tension perpendicular to surface [internal bond (IB)] test has been used as an important indicator of board quality in both production and utilization. It provides direct information on adhesion between wood components and the bonding agent and shows the location of the weakest plane within the cross-section of the product. Thus the IB test is generally considered the most significant for determining composite quality (Kyoken, 1986). This mode of testing is particularly relevant in the contact of the present research area which concerns considerations of stress balances within the panel during pressing and upon press opening. Stresses on adhesive bonds principally act in the perpendicular direction (resulting from internal vapor pressure and residual elasticity of the mat).

Simplified and fast methods for measuring the internal bond strength of composite panels have been developed by some workers (Lehmann,1965; Shen, Carroll, 1969; Gandent,1978). Strickler (1959) also studied the effect of using particleboard furnishes of differing mean moisture contents (6%, 9% and 12%). When the pressing platen temperature was not changed, the maximum value of internal bond strength was achieved when the initial moisture content of the mat was 9%.

The X-ray spectrometer, infrared analyzer and differential scanning calorimeter (DSC) have also been used to study surface reactions during bonding and resin polymerization (Chow,1976,1979; Kaspen, Chow,1980; Kelley, et al.1983).

The above and other similar techniques provide no indication of

rates of strength development, but only final board or bond performance. They certainly do not indicate bond strengths at different stages of cure - from the liquid or powder to the fully cured state.

2.5.2. Direct measurement of curing rates

No direct research of adhesive strength development rates appears to have been reported until that of Humphrey and Bolton in 1979. This enabled bond strength development to be inferred directly and was used to investigate urea formaldehyde resin to wood bond formation under laboratory conditions. The method has solved problems which the other methods could not avoid in the study of bonding kinetics. As has been pointed out in chapter I, bonds can be formed under highly controlled conditions of temperature and immediately tested in tension. The derived data was used by Humphrey to predict bond strength development within mats of flakeboard by using a computer simulation system (Humphrey,1979,1982,1985). These methods are still being improved and the present work considerably extends to use of the method. Figure 2-19 shows a typical bond strength development curve derived using this test method.

Repetition of many such sets of tests for a number of differing steady-state temperatures enables a family of such curves to be constructed. The effect of temperature on bonding rate may then be analyzed numerically. Figure 2-20. shows a family of strength development curves for different temperature.
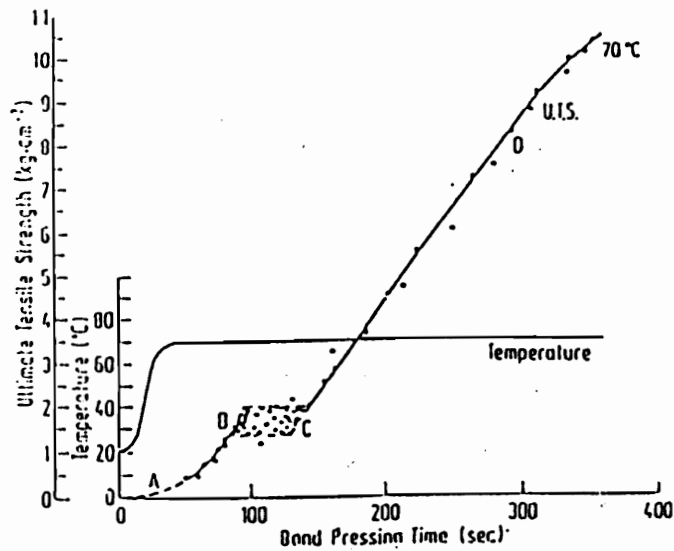
Figure 2-19. A typical bond strength-time curve with glueline temperature curve (from Humphrey and Bolton,1979)
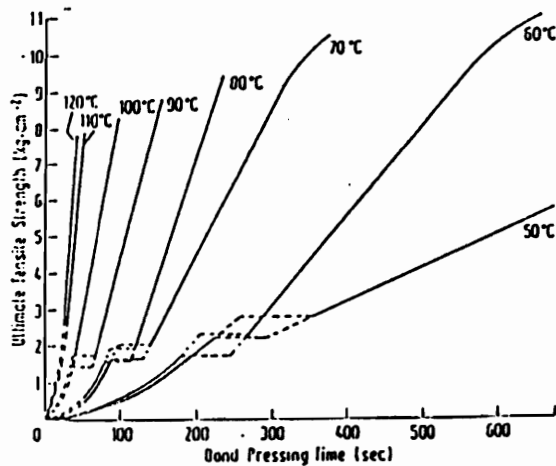
Figure 2-20. A family of strength development curves for different steady-state temperatures (from Humphrey and Bolton,1979)

The rate of cure of thermosetting resins is clearly dependent on temperature. It is, however, also likely that moisture may play a role in affecting adhesion kinetics. It has already been poited out (section 2.2) that temperature and moisture content are a function of heat and mass transfer within composites during pressing. Preliminary measurements made by Humphrey and Bolton (1979) on bonds formed at two different moisture contents suggest that adhesion kinetics are indeed dependent on moisture content. see Figure 2-21.
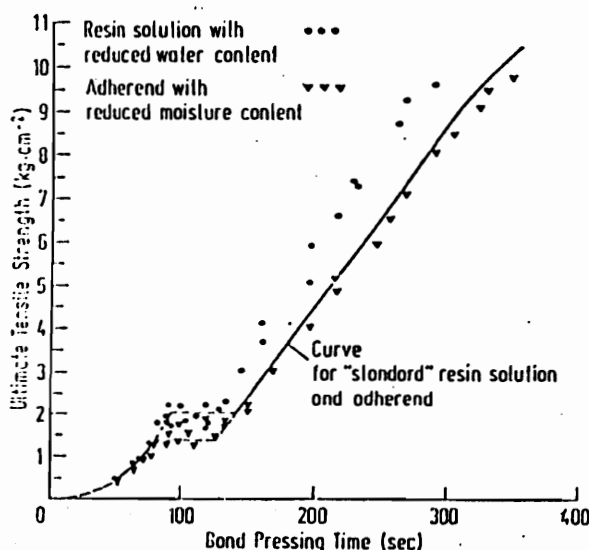
Figure 2-21. Effect of wood-resin system moisture content on strength development at 70 C (from Humphrey and Bolton,1979)

The bond strength development curves consistently show a two stage cure taking place under varying heating conditions. During the initial cure stage, a limited increase in bond strength is observed. This is followed by a decrease or halt in bond formation before rapid strength development begins in the second stage.

The Torsional Braid Analysis (TBA) technique was developed and used by Steiner and Worren (1981,1987) to study the rheology of adhesive cure and some non-continuous cure behavior during the early stages of cure were observed. see Figure 2-22.
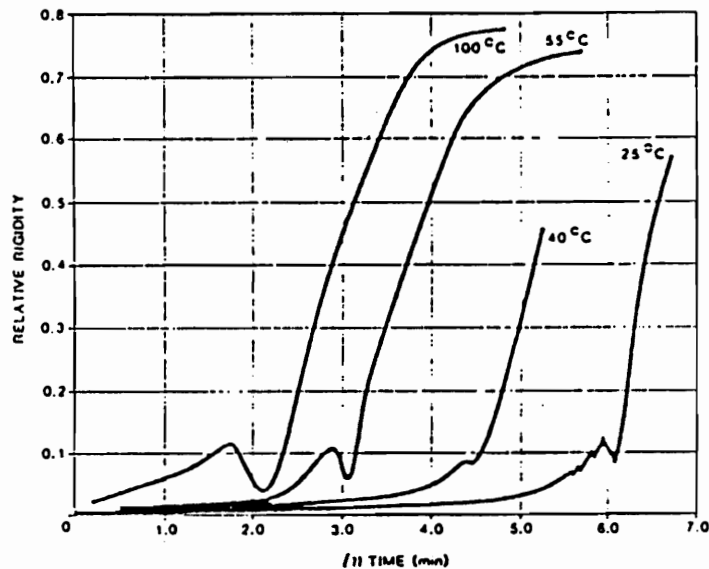
Figure 2-22. TBA cure rigidity profile of a UF laminating adhesive cured isothermally at various temperatures (from Steiner,1981)

This method (TBA) is useful for indicating the early stages of adhesive cure. The work is mostly limited to UF adhesive and it was not possible to include wood material in the test. It is not able to study the effects on the wood-adhesive interface. The complex interactions between wood and adhesive, and the combined effects of moisture content and temperature are not accessible.

Research to be undertaken in the present project will attempt to expand the principle of the method described by Humphrey and Bolton (1979) to account for the combined effects of both temperature and moisture content.

CHAPTER III

EXPERIMENTAL METHODS

3.1. The research approach

Using simulation techniques, it has been possible to predict the variation of temperature and moisture content throughout dry formed wood based composite panels as pressing proceeds (Humphrey,1982; Humphrey and Bolton,1987). It is clear from the preceding discussion that bond strength development plays an important role in the process and its prediction is necessary for process optimization. It has already been demonstrated that the rate of bond strength development is highly dependent on temperature. It is also clear, however, that moisture content in the vicinity of adhesive bonds influences strength development. The methods described here are designed to provide a quantitative understanding of how both temperature and moisture content effect bonding kinetics. There are many factors which together influence bond strength development, but not every factor plays an equally important role. Only those factors that have a significant effect on the behaviour of the system should be included in models. Other, less significant factors must then be held constant throughout our experiment.

Adhesion within wood composites is influenced by many factors (such as mat forming methods, pressing cycle, temperature, and moisture content). If the composite system could be analyzed by micro-mechanical methods (otherwise termed elemental unit analysis) the complex system

may be simplified. In the present study, this unit system consists of one glueline between two small pieces of wood. This approach can be used in fundamental studies of the bonding kinetics operative within composites such as plywood, waferboard and flakeboard. Figure 3-1 shows schematically one such element or unit.
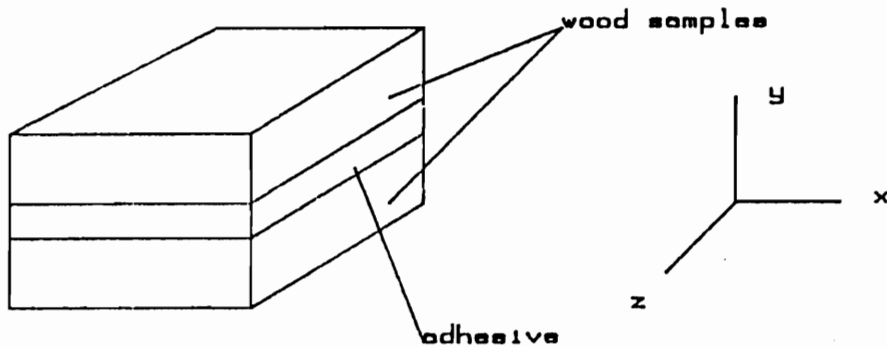
Figure 3-1. The basic unit for analysis

The present experiment was designed to study rates of bond formation under a range of temperature and moisture content conditions. First, the temperature was held constant and the rate of bond formation was measured for a range of moisture contents. Then, the moisture content of specimens was held constant and a group of bonds were similarly formed and tested at a range of temperatures. The combined effects of temperature and moisture content on bonding rates were

investigated in this way. The experiment was specially designed to provide data which can, in future work, be used in simulation models of hot pressing composites.

The circular-disk tension test was adopted here for it results in fracture occurring in the interface zone, and does not contain any square corners to perturb behavior of bond strength development and testing. Loading on bonds within actual panels are in this mode (particularly upon press opening) so results should be directly applicable in the simulations to follow in later work.
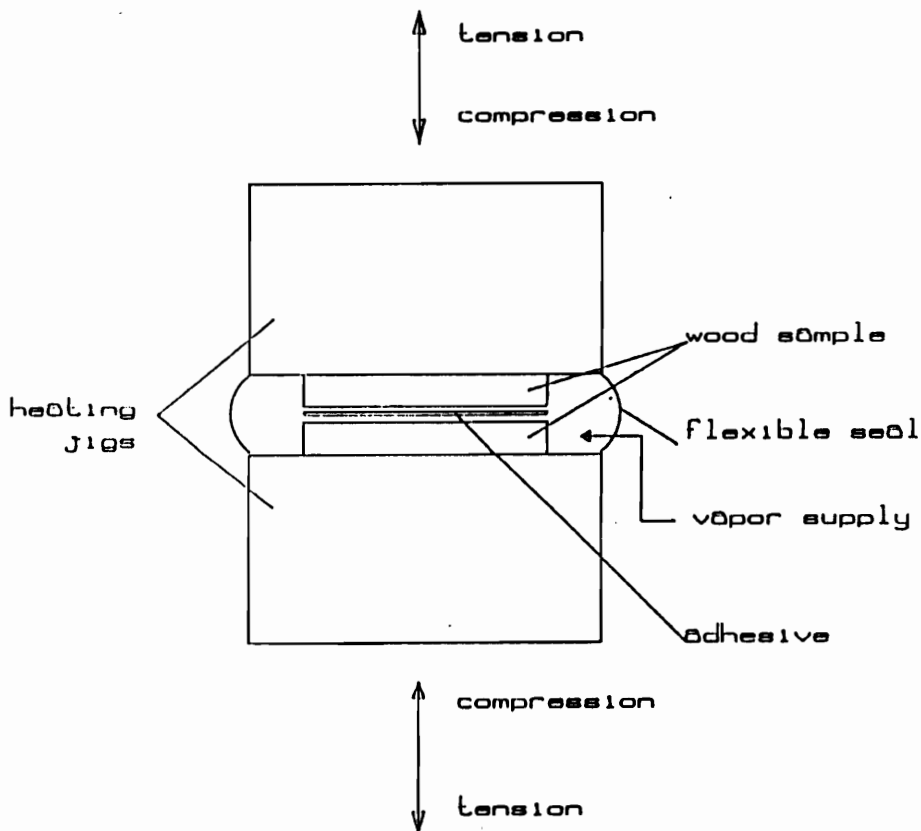
Figure 3-2. The basic principle of the test method

The basic principle of the test is shown as Figure 3-2. This apparatus effectively consists of a small circular hot press with the provision for accurate load and temperature control. In addition, peripheral sealing of the platens enables atmospheres of controlled RH and temperature to be injected and maintained around the specimen. Automatic clamping of specimens in the press enables both compressive and tensile loads to be applied. Details of the design of this experiment are provided in sections to follow.

3.2. The testing sequence

Circular Douglas-fir (Pseudotsuga Mensiesi) disks 38 mm diameter and 1 mm thick were surface sanded and bonded to aluminum mounting disks using high temperature epoxy adhesive. The specimens were then put in a climatic cabinet to achieve the required wood MC. Powdered PF resin was uniformly applied to the wood sample surfaces. Powdered adhesive was used to enable moisture content in the vicinity of the adhesive bond to be accurately controlled. The use of liquid resin in preliminary trials did not enable accurate moisture control to be achieved. The quantity of adhesive (spread rate) corresponded to that typically applied to the surface of flakes used in composite panel manufacture. This value was estimated by calculating the approximate surface area of flakes per unit volume of the panel, in conjunction with the known resin solids in such a panel.

Following resin application, the two wood disks were immediately mounted on the test system - the heated rams having first been set to the required temperature. The jigs were then closed to a pre-determined

pressure at a controlled rate. In this way, the test bonds quickly reached steady-state temperature (that of the platen) as heat was rapidly conducted through the thin wood disk. At the same time, vapor of the required RH and temperature from the pre-adjusted supply system was injected around the specimens. This combination of RH and temperature corresponded to the atmosphere which produces an equilibrium moisture content the same as that of the pre-conditioned wood sample.

The specially designed flexible peripheral sealing system was inflated to keep the system closed for controlling the environment for each test. Towards the end of the pre-selected bond forming period and prior to testing, the pneumatic disk clamping system was activated. After the selected hot-pressing time, the strength of the bond was tested immediately in tensile mode by reversal of the load applied by the testing machine.

Repetition of this procedure for different pressing times enabled the development of bond strength during steady-state forming conditions to be evaluated. New wood sample disks were prepared for each test. Results were specific to the material, adhesive, temperature, moisture content, and platen pressure used. The sequence of operations is outlined in Figure 3-3. Sets of approximately forty test disks were prepared together. This enabled twenty measurements to be completed in any one sequence of tests.

As already stated, each set of tests was conducted under controlled conditions of temperature and moisture content while all other conditions were held constant. This enabled the combined influence of temperature and moisture content on each stage of bond formation to be

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studied quantitatively.

```
┌─────────────────────────┐        ┌─────────────────────────┐
│ Wood disk manufacture   │────┬───│ Aluminum disk cleaning  │
└─────────────────────────┘    │   └─────────────────────────┘
                               ▼
              ┌──────────────────────────────────┐
              │ Bond wood disks to aluminum disks │
              └──────────────────────────────────┘
                               │
                               ▼
          ┌──────────────────────────────────────────┐
          │ Condition wood to required moisture content │
          └──────────────────────────────────────────┘
                               │
┌─────────────────────────┐    │   ┌─────────────────────────┐
│ Pre-heat test system    │    │   │ Pre-set Vapor production │
│ (jigs) to required      │────┼───│ system to required       │
│ temperature             │    │   │ temperature and relative │
└─────────────────────────┘    │   │ humidity                 │
                               ▼   └─────────────────────────┘
       ┌───────────────────────────────────────────────┐
       │ Apply powder PF adhesive to specimen surfaces   │
       └───────────────────────────────────────────────┘
                               │
                               ▼
          ┌──────────────────────────────────┐
          │ Mount specimens in test system    │
          └──────────────────────────────────┘
                               │
                               ▼
              ┌─────────────────────┐
              │ Close hot press      │
              └─────────────────────┘
                               │
┌─────────────────────────┐    │   ┌─────────────────────────┐
│ Activate peripheral      │────┼───│ Inject vapor             │
│ sealing                  │    │   └─────────────────────────┘
└─────────────────────────┘    ▼
       ┌───────────────────────────────────────────────┐
       │ Bond formation (hot-pressing)                   │
       │ (Temperature and moisture content control)      │
       └───────────────────────────────────────────────┘
                               │
                               ▼
          ┌──────────────────────────────────┐
          │ Activate disk clamping mechanism  │
          └──────────────────────────────────┘
                               │
                               ▼
          ┌──────────────────────────────────┐
          │ Tension test for bond strength    │
          │ (after required forming time)     │
          └──────────────────────────────────┘
                               │
                               ▼
          ┌──────────────────────────────────┐
          │ Record ultimate bond strength     │
          └──────────────────────────────────┘
                               │
                               ▼
              ┌─────────────────────┐
              │ Remove specimens     │
              └─────────────────────┘
```

Figure 3-3. The experimental procedure

3.3. Equipment design

3.3.1. Introduction

The follow functions are required of the equipment:

-- Control of temperatures up to 180 ^{O}C ($\pm$1 ^{O}C) within the glue bond.

-- Maintenance of constant moisture content within the bond forming chamber.

-- The provision of compressive pressure (bond formation) and tension (tensile testing) for selected time intervals. A smooth and rapid transition from bond formation to bond testing modes must be achieved.

-- Wood specimens and adhesive should be as uniform as possible.

New miniature equipment had to be designed and manufactured to meet the requirements. The function of this equipment is to keep the total test system in accurately controlled steady-state conditions of temperature and moisture content throughout the cross section of the specimens as bonds are formed. Boundary effects and some unsteady-state factors have, therefore, been reduced to a minimum. The system consists of the following parts:

-- Pressing jigs

-- Heating and heating control systems

-- Vapor production, control and injecting systems

-- Flexible platen sealing system

-- Test disk restraining (fixing) system

-- Specimens pretreatment system

The equipment has been designed to enable a wide range of testing situations on many different material types to be carried out. The specification listed below for the equipment therefore covers ranges wider than those required solely for the present work:

Platen temperature: 25 ---- 180 ^{O}C.

Relative humidity of injected vapor: 3 ---- 100 %

Maximum compressive pressure: 20 kg/cm^2

Maximum tensile pressure: 18 kg/cm^2

3.3.2. The testing jigs

The jigs are used first to form and then to immediately test bonds. The functions of the jigs are listed below:

-- compressive loading (bond formation)

-- heat transfer and control to glue line

-- moisture content control of bond

-- clamping specimen to jigs (for tensile testing)

-- tensile loading (bond testing)

The jigs are rigid so that they can withstand applied loads without significant compressive or tensile distortion. The platens must also provide good conductivity of heat to the specimens. The primary

provide good conductivity of heat to the specimens. The primary functions of the jig arrangement is represented schematically as Figure 3-4.
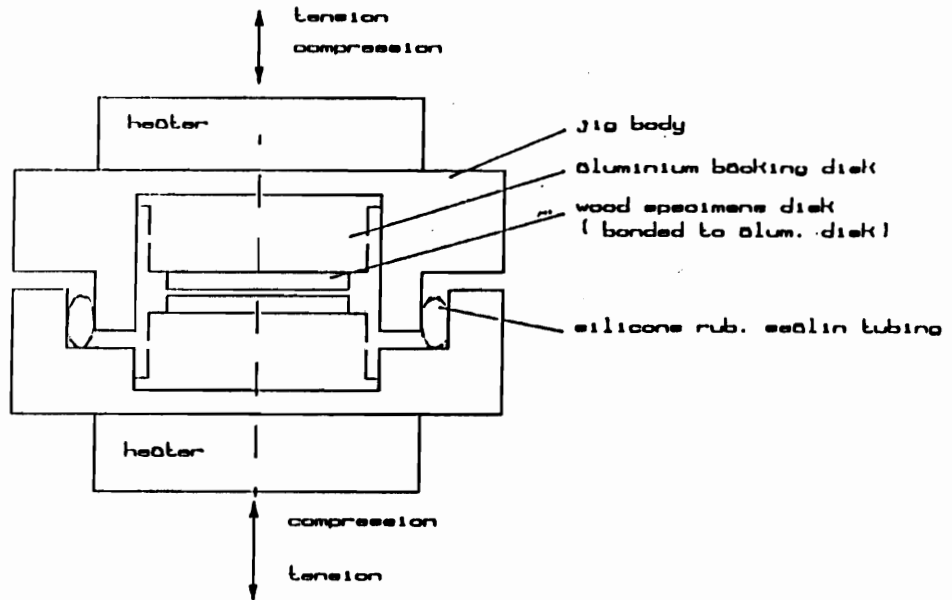
Figure 3-4. Primary functions of the circular testing jigs (specimens in position but prior to press closure)

3.3.3. The heating system and temperature control

The objective was to form and test bonds under as uniform temperatures as possible. The system required enough heat capacity to avoid significant decreases of temperature when the cold wood samples and associated aluminum disks were added. Thermocouple feedback signals were used to control the electric power with the aid of three term temperature controllers.

The principle components of the temperature control system is represented schematically as Figure 3-5:

Figure 3-5. Heating and temperature control

To affect heating of the samples quickly once they are mounted in the jigs and for convenient operation, the following issues were of concern:

-- good heat conduction from the heaters throughout the aluminum blocks.

-- reasonably rapid attainment of set temperatures of the jigs over the range of approximately 30 to 180 ºC.

-- uniform temperature distribution in cross-sections of jigs.

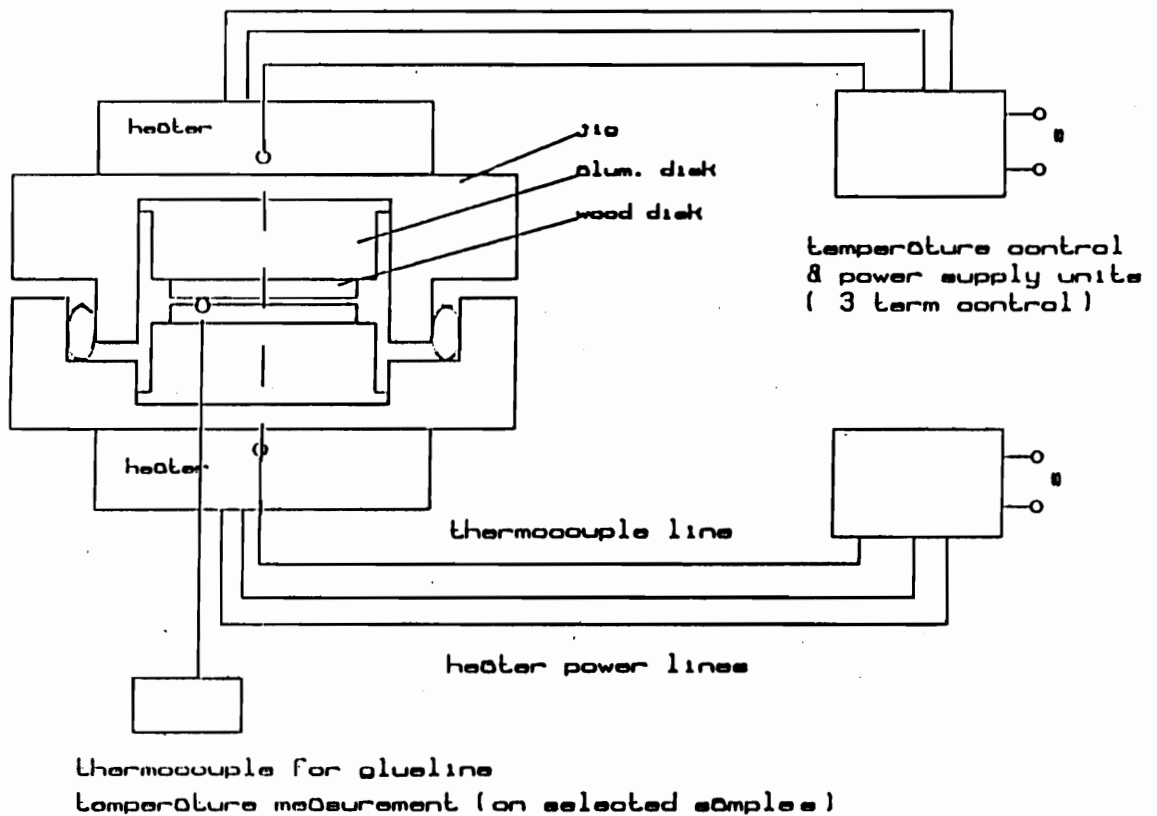Here, differences between the temperature of the jigs and that of the glueline as bond pressing proceeds must be considered. When the sample were first put into the jigs, heat was transferred very quickly from the jigs through the wood to the adhesive. Clearly, a temperature gradient is established within the samples at the early stages of pressing. But after a short time, the glueline is raised to the same temperature as the jigs and from then on the temperature remains quite constant ($\pm 0.5^{\circ}$C). The delay in attainment of steady-state temperature influences the bond forming process. Special care was taken in the design of the apparatus and specimens to maximize heat transfer so that only a very short time elapsed before test temperatures were reached. The form of a typical glue line heating curve is shown as Figure 3-6. Curves specific to each pressing temperature used will be presented later in the thesis.
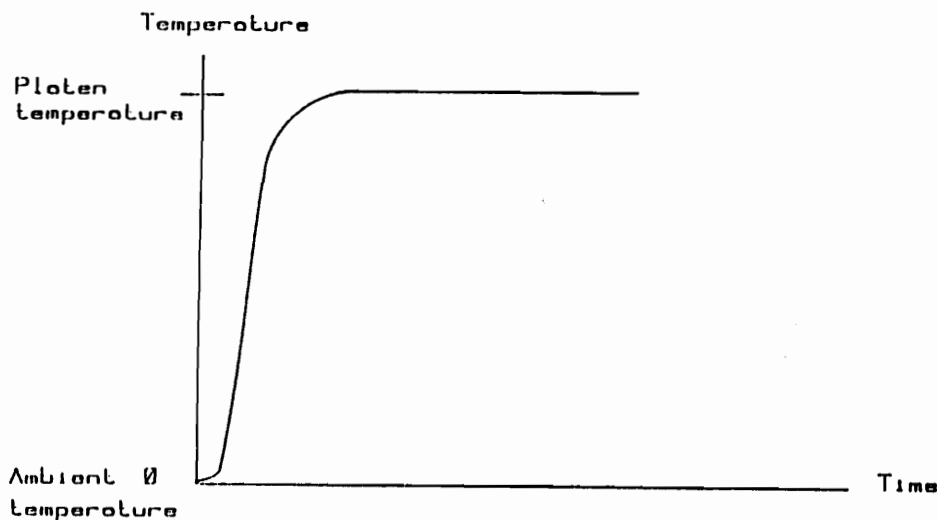
Figure 3-6. Difference of temperature between jigs and glueline as bond formation proceeds

3.3.4 Moisture content control and the vapor production system

Two components were designed to affect control of moisture conditions during testing. One was the vapor supply system, the other was the sealing system to contain vapor around the bond as it was being formed.

a. The vapor system:

The function of this system was to produce water vapor of differing RH and temperature, to inject between the jigs and around the specimens so that their moisture content could be kept constant during bond formation. The system itself is diagrammed as Figure 3-7. and a photograph appears as Figure 3-8.
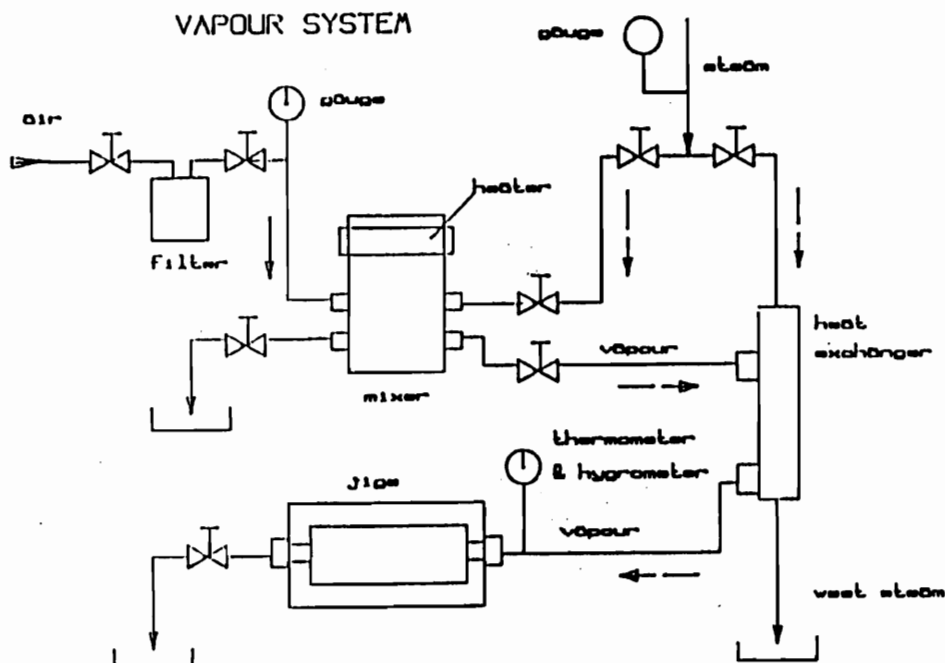
Figure 3-7. A schematic of the vapor production system

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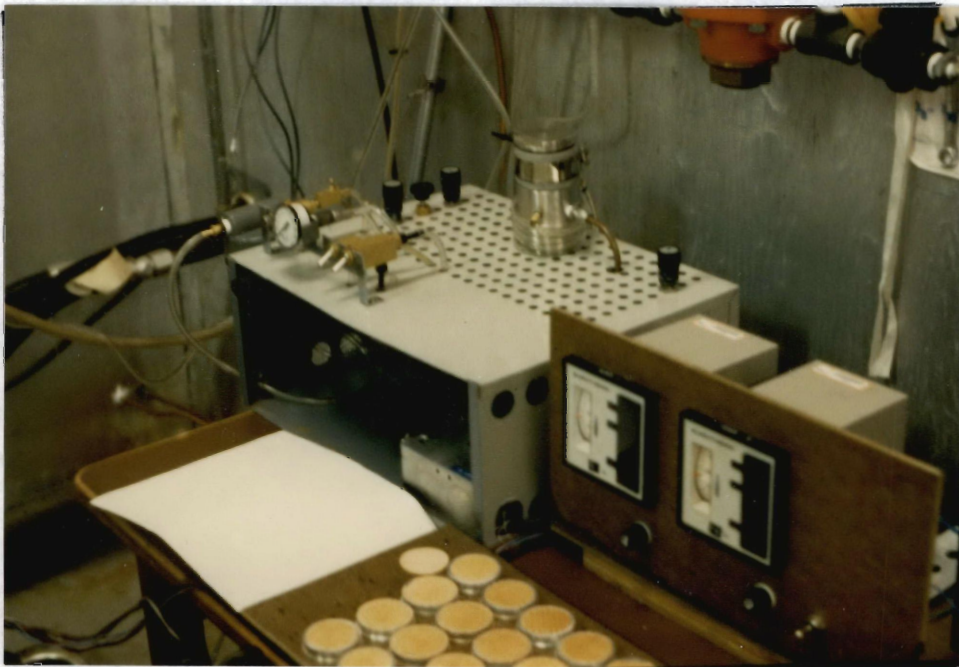
Figure 3-8. The photograph of the vapor production system

The system successfully produces vapor of different conditions (temperature, relative humidity and pressure). The equipment can work under the following condition:

1. temperature: 25 --- 125°C.

2. relative humidity: 3% --- 100%.

3. gage pressure: 0 --- 6 kg/cm^2.

b. The sealing system:

Horizontal boundary conditions around the periphery of the test bond were controlled by using a specially developed flexible sealing system which prevented the escape of vapor. The arrangement for peripheral sealing is shown as Figure 3-9.
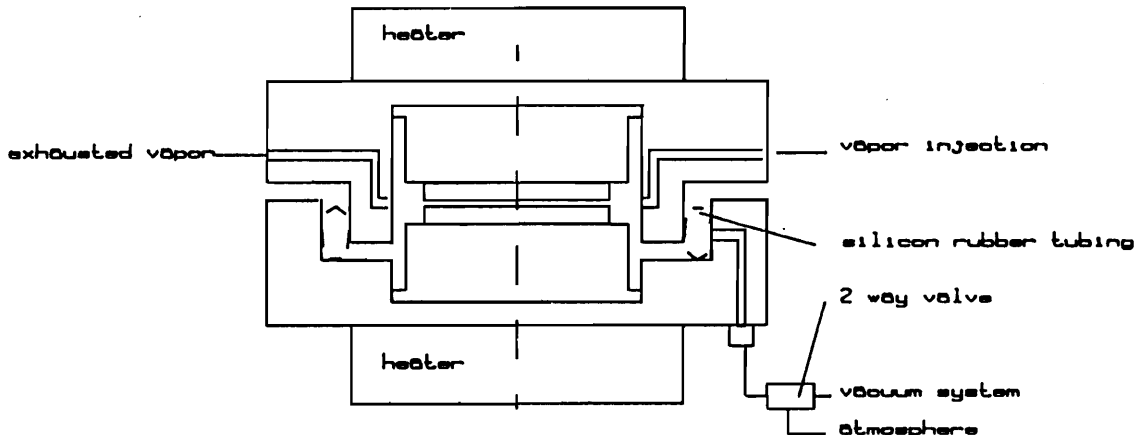
Figure 3-9. Boundary control with the sealing system

To enable the jigs to close freely, the silicone rubber tube (forming a diaphragm) was evacuated. The tubes' wall was sufficiently flexible to result in its collapse. When the jigs were closed, the vacuum was vented to atmosphere so that the silicon rubber tubing recovered its original shape and sealing between the two rams was affected. The original design included the application of compressed air to the sealing tube but this was found to be unnecessary; the natural elasticity of the tubes' wall was sufficient to contain internal vapor pressures used in the present experiments. If, in future work, experiments are conducted at higher pressures, pressurized (inflated) sealing may prove necessary.

Immediately upon sealing, the vapor of pre-selected condition (RH, temperature and pressure) was injected into the jigs around the testing specimens. In this way, the edge of the specimens were maintained at the same temperature and moisture content as in other parts of their volume. The experiments could, therefore, be conducted under steady-state conditions for most of the bond forming period.

3.3.5. Specimen treatment and fixing

a.   Pre-mounting the wood disks:

The wood disks were first bonded onto the specially manufactured aluminum alloy disks and it was important to produce a wood to metal bond stronger than the corresponding PF bond strength at elevated temperature. A high temperature resistant epoxy adhesive (Araldite 2004) was used here. A clamping jig was designed to ensure even

pressure over the aluminum alloy disk as they cured. About forth such specimens were prepared at a time. On subsequent completion of each test the wood and epoxy residues were removed (faced off) from each aluminum alloy disk using a small lathe. A cross-section through one prepared specimen (wood disk bonded to aluminum) is shown as Figure 3-10. and a photograph of some disks is shown as Figure 3-11.
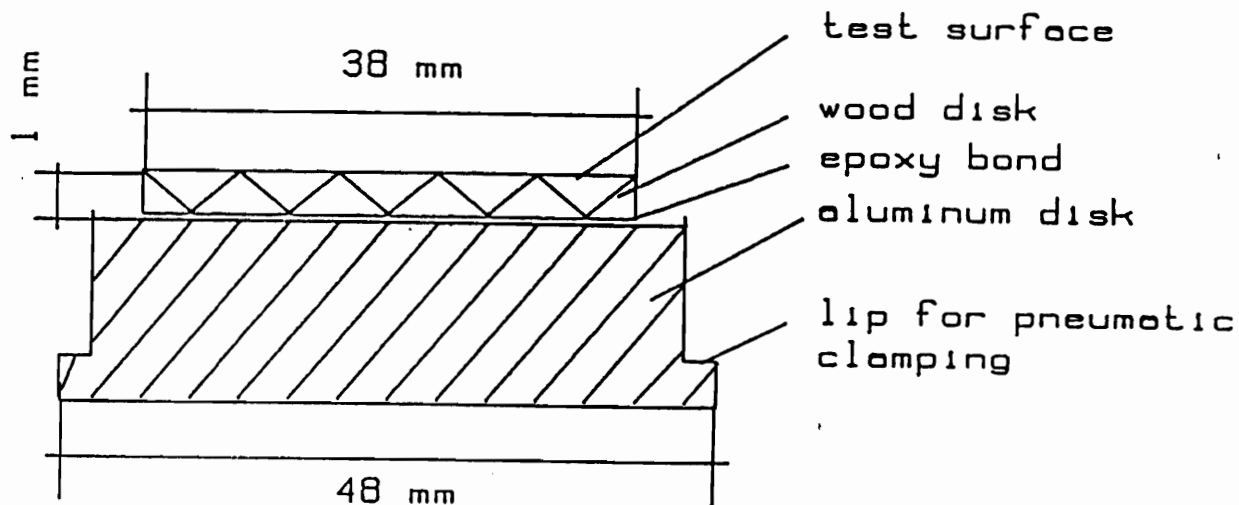
Figure 3-10. Cross-section through wood disk bonded onto aluminium backing disk

Figure 3-11. Photograph of some typical specimens

b.   Conditioning the specimens to appropriate moisture contents:

The mounted specimens were placed in either a climatic cabinet or one of a number of different conditioning rooms to adjust the moisture content of the wood to the required value.

c.   Restraining the specimens in the testing jigs:

The specimens were held in the jigs by means of a specially designed piston locking system which was driven by compressed air. When the air valve was activated, 12 pistons (6 pistons for each of the two

jigs) gripped the aluminum disks around their periphery in readiness for tensile testing of the bond. The aluminium disks were manufactured with a lip into which the piston rods located. After each test, the air supply was switched off and vented to atmosphere and the pistons automatically retracted by spring return. This locking arrangement is represented in Figure 3-12. and a photograph of the pneumatic disk clamping system is shown in Figure 3-13.
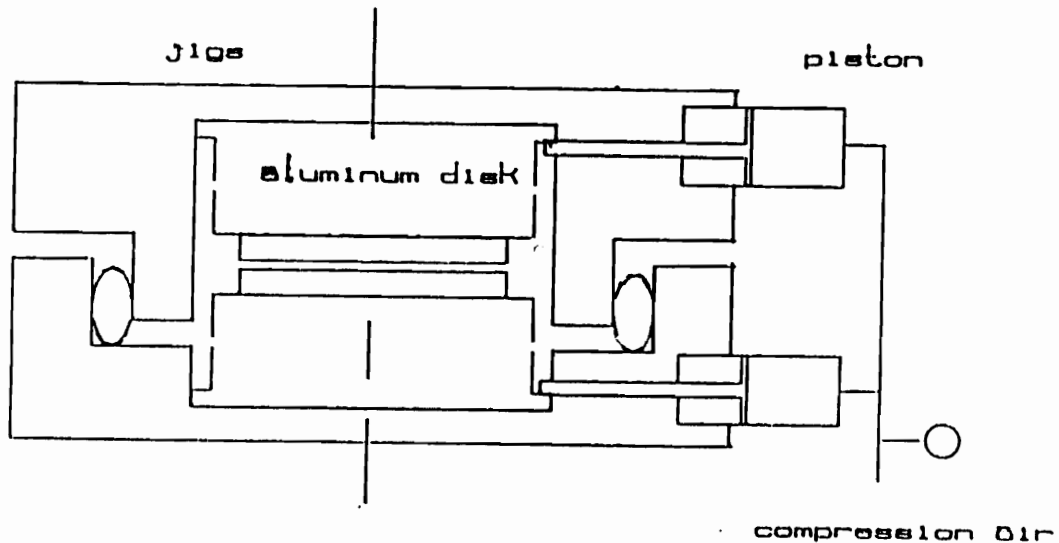
Figure 3-12. Partial detail of the pneumatic disk clamping system
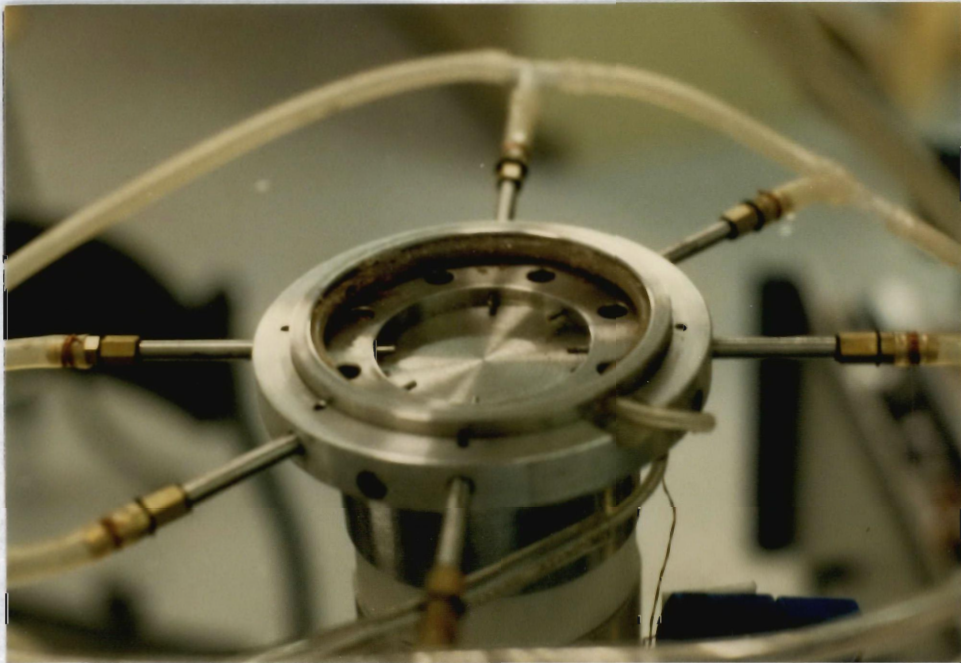
Figure 3-13. A photograph of the pneumatic disk clamping system

The overall testing arrangement is shown as Figure 3-14, Figure 3-15 and photographically as Figure 3-16.
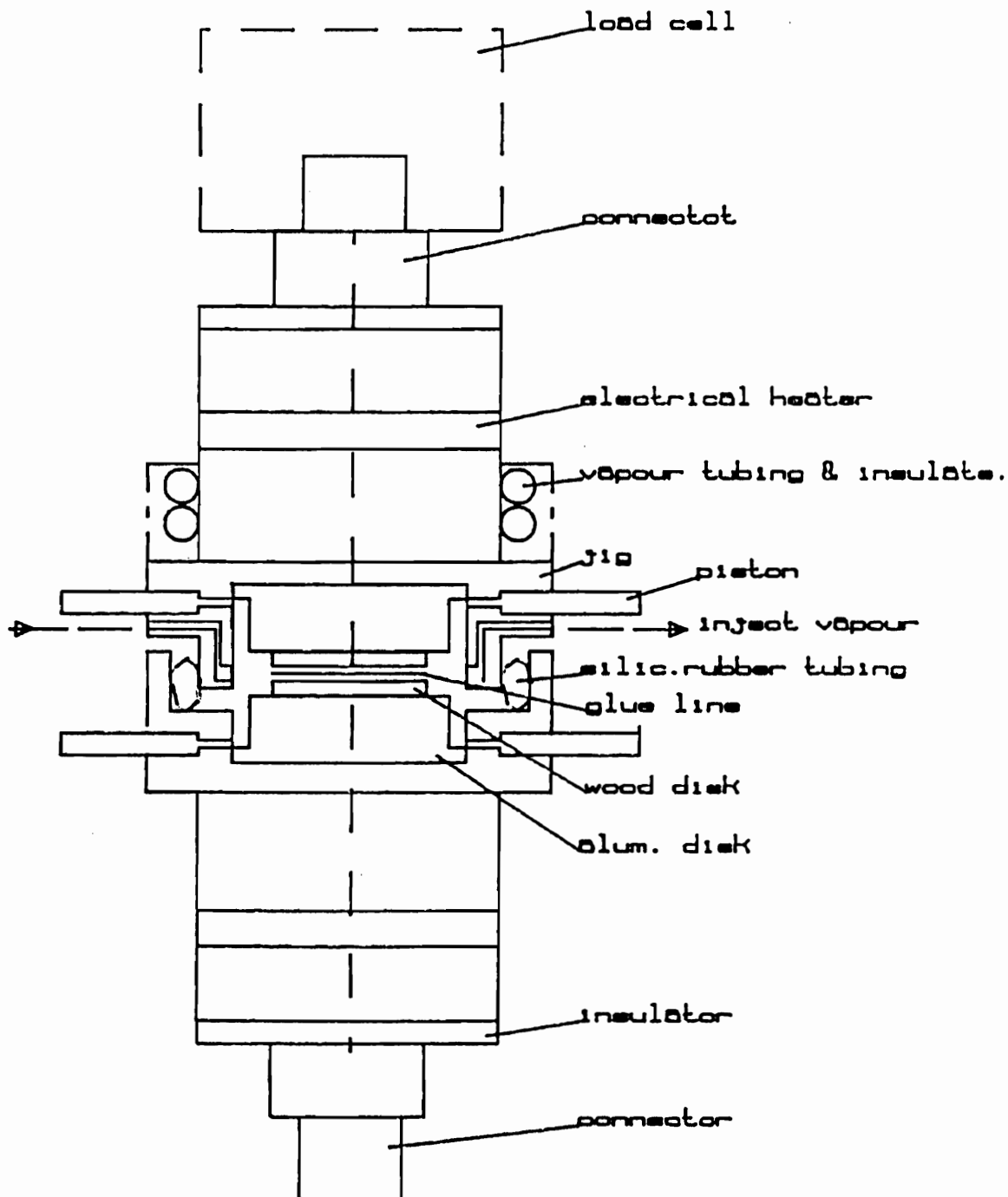
Figure 3-14. The overall experimental assembly
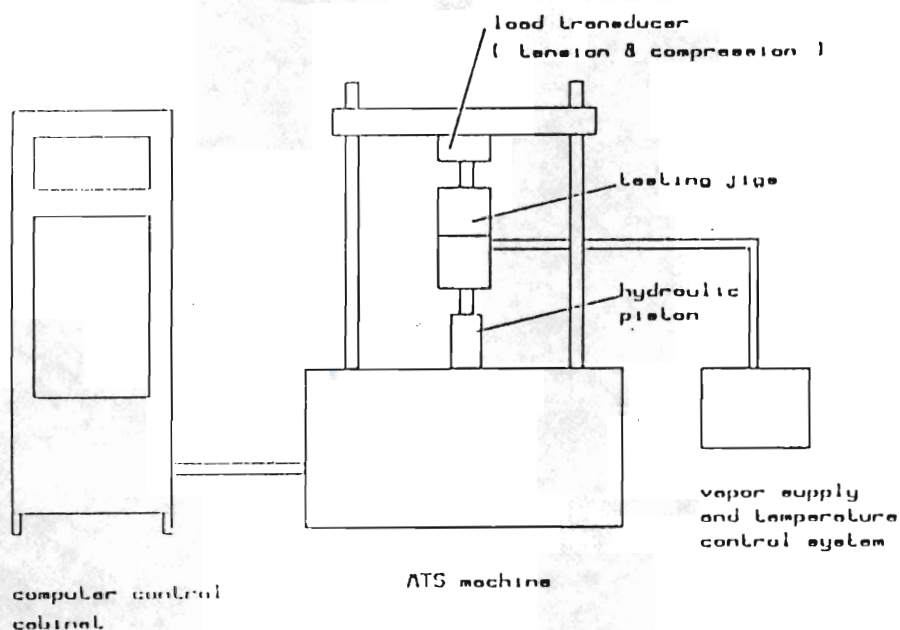
Figure 3-15. Equipment mounted on the machine (MTS)

Figure 3-16. A photograph of equipment mounted on the machine (MTS)

3.4. Experimental parameters and derived data

3.4.1. Raw material

Douglas fir (Pseudotsuga Menseixi) was used in this experiment because it is commonly used for wood composites in Oregon and its properties and structure are more clearly understood then most other species. Quarter sawn veneer was parallel sliced to a thickness of 1 mm and kept in the standard room (21 $^{\circ}$C and 65 % RH) to enable uniform moisture content and stress relaxation to be achieved.

The adhesive used was phenol formaldehyde in powdered form which was donated by Bakalite Thermosets Company (BRP-9246). This is a heat reactive, one step adhesive for use in the production of waferboard and OSB. It is designed to be used as the sole resin in a one-resin manufacturing process or as the surface resin in a two-resin process.

3.4.2. Testing parameters

In order to classify the experimental details, the numerical specifications of the test are presented in tabular form as Table 3.1.

System constants

Wood species ——————————— Douglas fir (Pseudotsuga Mensiexi)

Rings per cm ——————————— 3   rings/cm

Mean density (at 10/MC) ——————— 460 kg/m^2

Adhesive type ——————————— Phenol formaldehyde (Powdered from Badalite Co.)

Adhesive spread rate ——————— 100 grams/^{m2}

Wood disk diameter ——————— 38 mm

Wood disk thickness ————————— 1 mm

Compressive force (bond forming)- 14 kg/cm^2

Closing rate ——————————— 1 cm/s

Opening (testing) rate ————— 1 cm/s
(from full compressive load to failure)

Variable parameters

bond forming temperatures ——————— 90, 110, 115, 120 ^{o}C

Bond forming moisture contents ——— 4, 10, 16 % (oven dry wood)

Number of bond forming times

at each condition ———————————— Typically 7

Number of replications

at each forming time ———————— Typically 3

Table 3-1. Essential numerical information concerning raw material

and testing parameters

3.4.3. The presentation of derived data

For each bond forming condition (temperature, moisture content and pressing time), two or three replications were conducted. The data derived from all tests is presented as Appendix A. A pre-requisite of data interpretation was to plot replications for each temperature and moisture content combination on a separate graph relating measured bond strength to forming time. Following this , replicates for each time were averaged to derive the clearest trends possible between time and accumulated strength. Figures 3-17 through Figure 3-33 present raw data plots which are followed by averaged plots for each of the selected testing conditions in turn.

Ultimate load values have been corrected for bonding area and are presented in the units of 14 kg force per square centimeter. Bond forming time is measured from the instant the two bonding surfaces were brought together to when bonds failed.

Implications of these basic curves are discussed in chapter IV to follow.

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Figure 3-17. Bond strength values for different forming times at constant forming temperature of 90 °C and moisture content of 10 %.

Figure 3-18. Averaged bond strength values versus bond formation time measured at 90 °C temperature and 10 % moisture content.

Figure 3-19. Bond strength values for different forming times at constant forming temperature of 110 °C and moisture content of 10 %.

Figure 3-20. Averaged bond strength values versus bond formation time measured at 110 °C temperature and 10 % moisture content.

Figure 3-21. Bond strength values for different forming times at constant forming temperature of 115 °C and moisture content of 10 %.

Figure 3-22. Averaged bond strength values versus bond formation time measured at 115 °C temperature and 10 % moisture content.
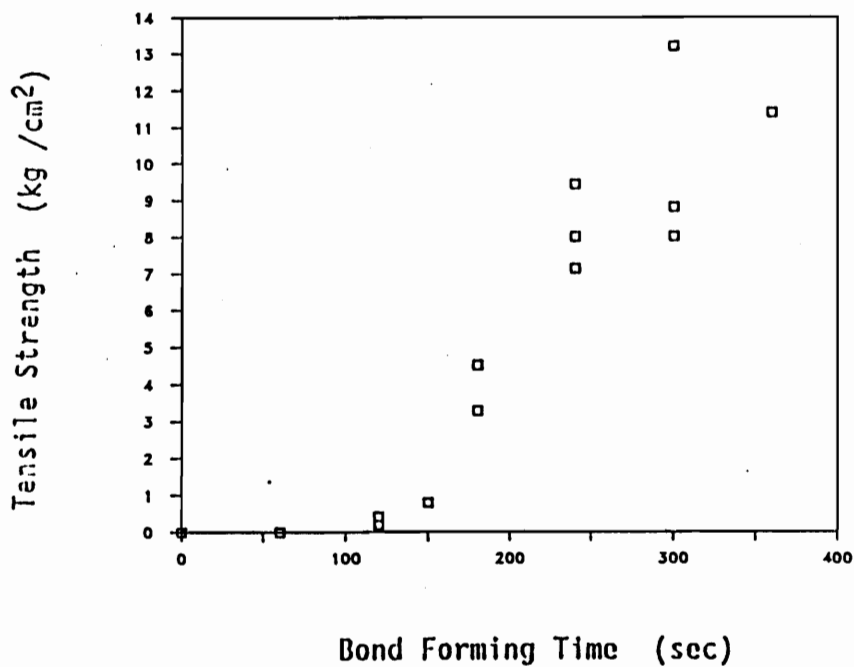
Figure 3-23. Bond strength values for different forming times at constant forming temperature of 120 °C and moisture content of 10 %.
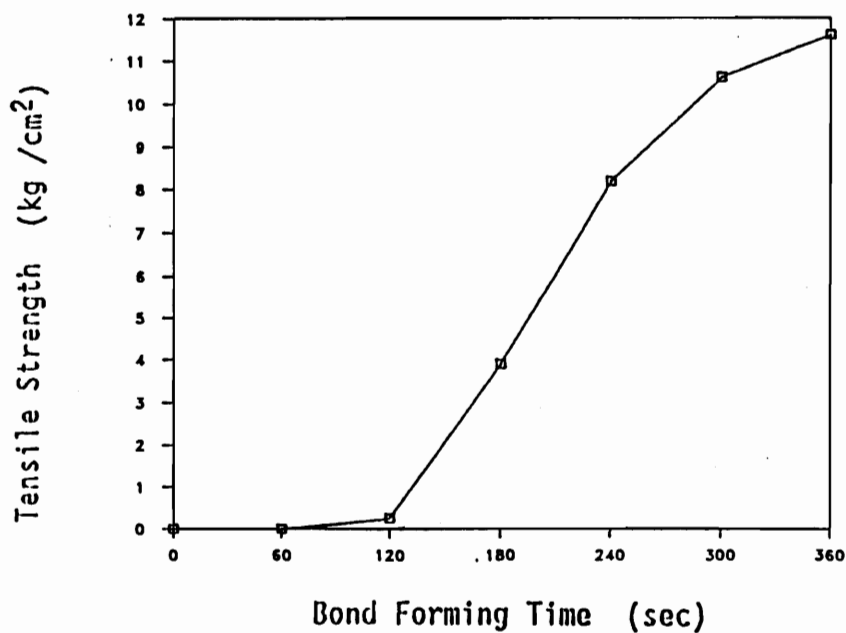
Figure 3-24. Averaged bond strength values versus bond formation time measured at 120 °C temperature and 10 % moisture content.
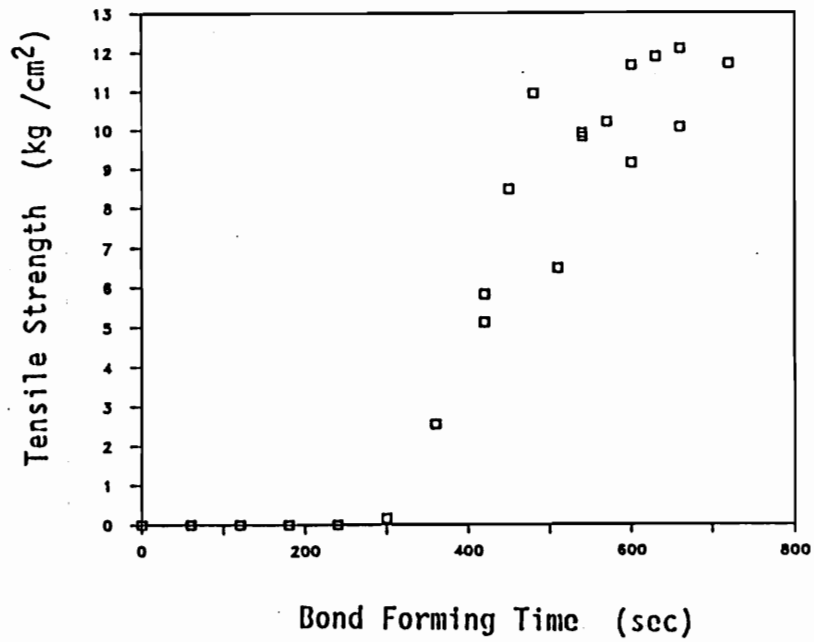
Figure 3-25. Bond strength values for different forming times at constant forming temperature of 110 °C and moisture content of 16 %.
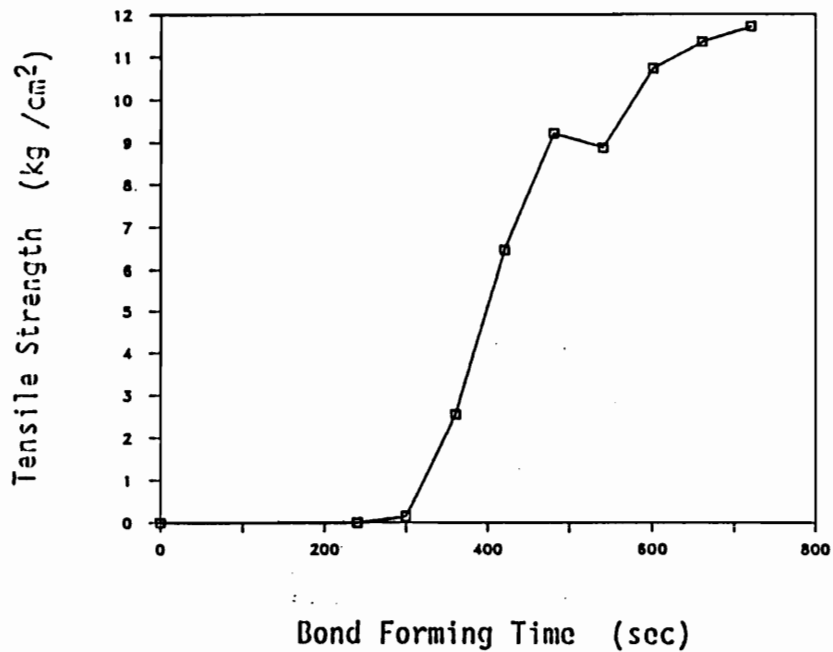
Figure 3-26. Averaged bond strength values versus bond formation time measured at 110 °C temperature and 16 % moisture content.
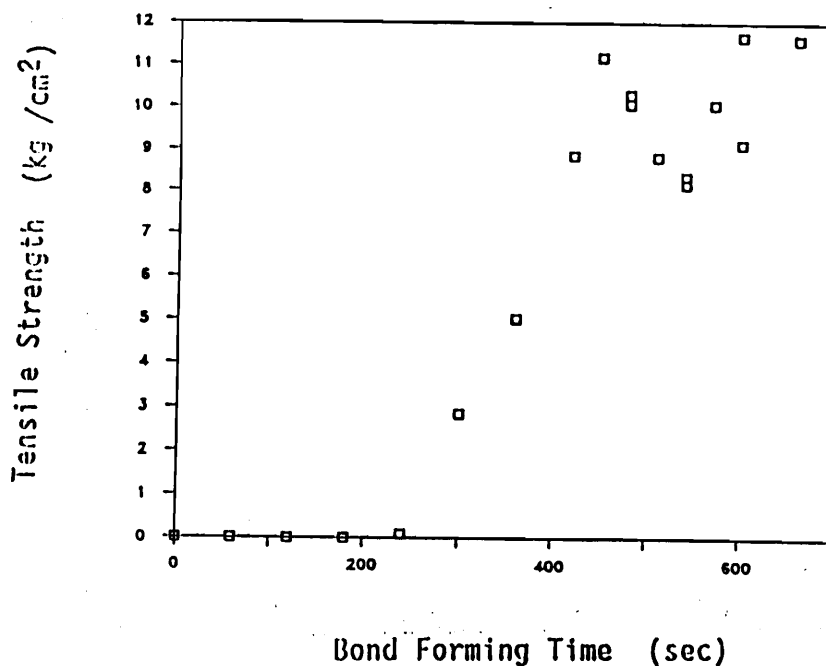
Figure 3-27. Bond strength values for different forming times at constant forming temperature of 115 °C and moisture content of 16 %.
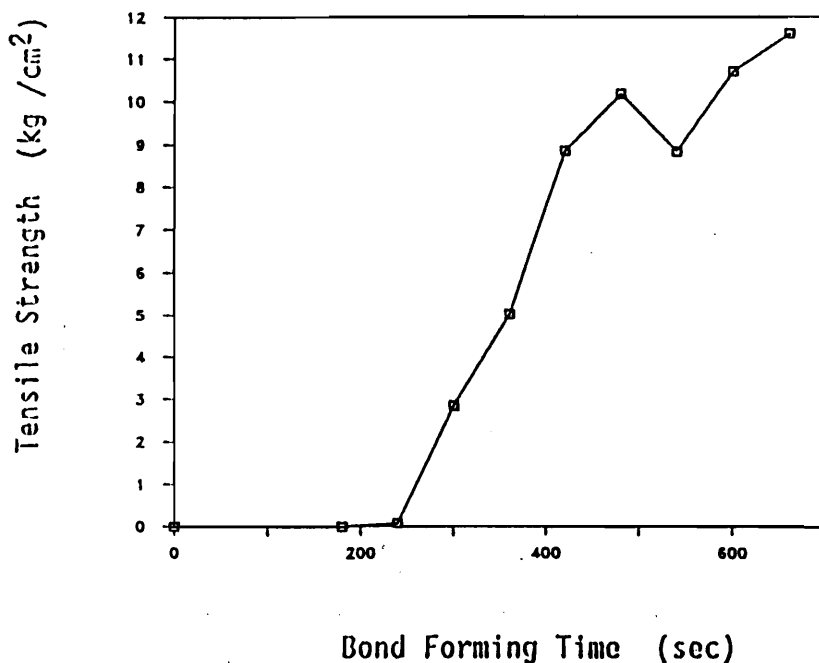
Figure 3-28. Averaged bond strength values versus bond formation time measured at 115 °C temperature and 16 % moisture content.

80
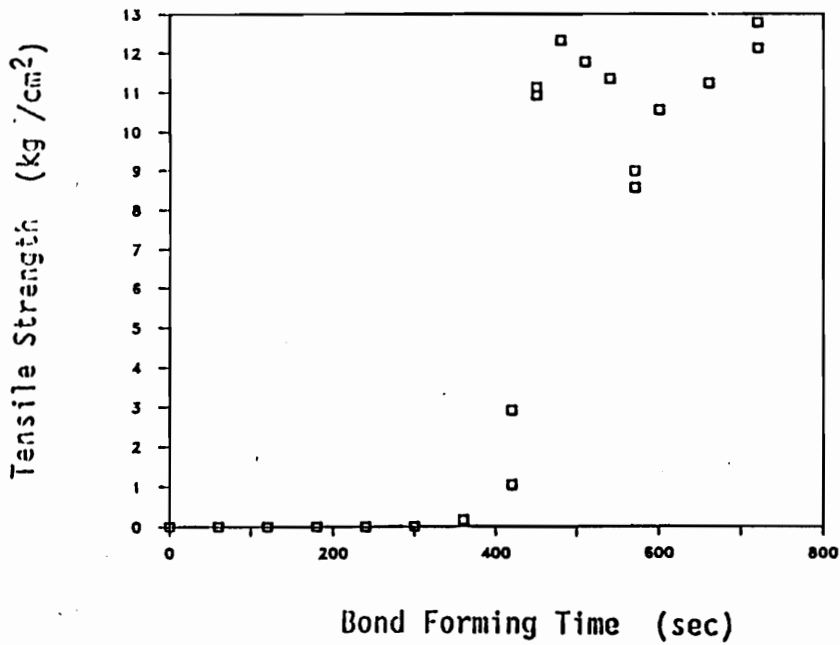
Figure 3-29. Bond strength values for different forming times at constant forming temperature of 110 °C and moisture content of 4 %.
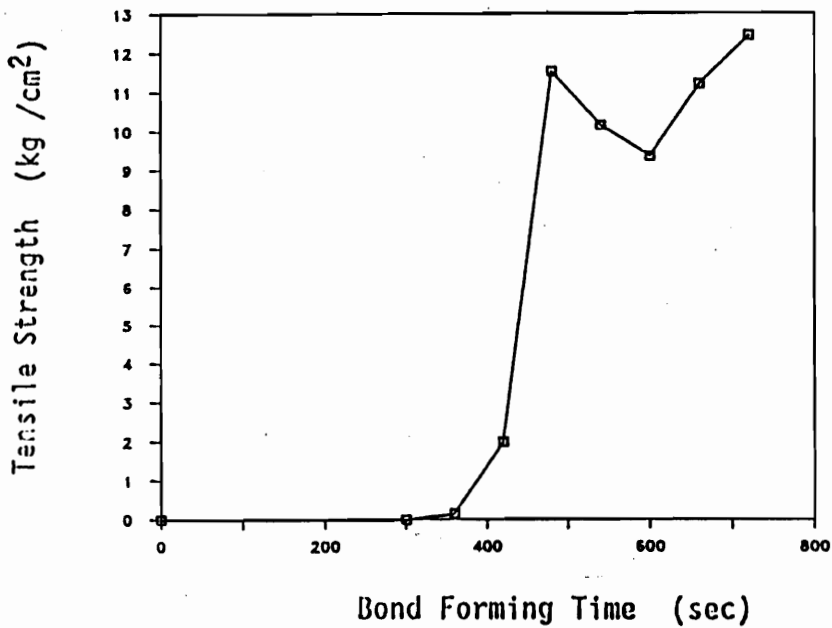
Figure 3-30. Averaged bond strength values versus bond formation time measured at 110 °C temperature and 4 % moisture content.
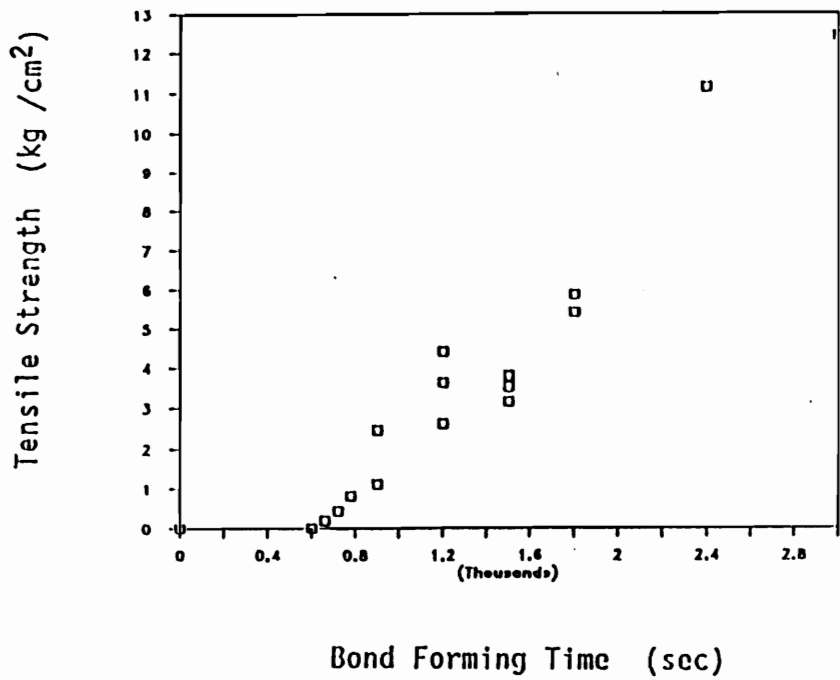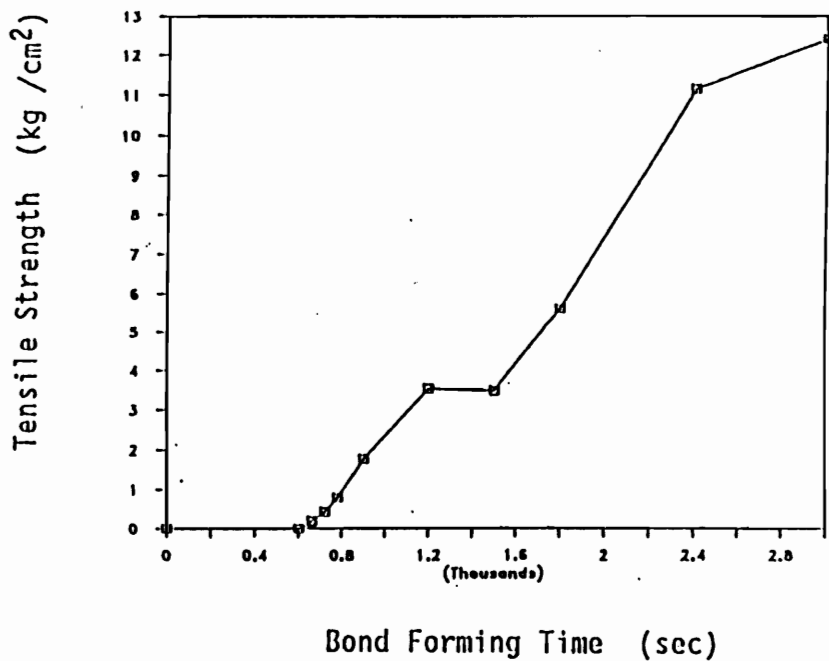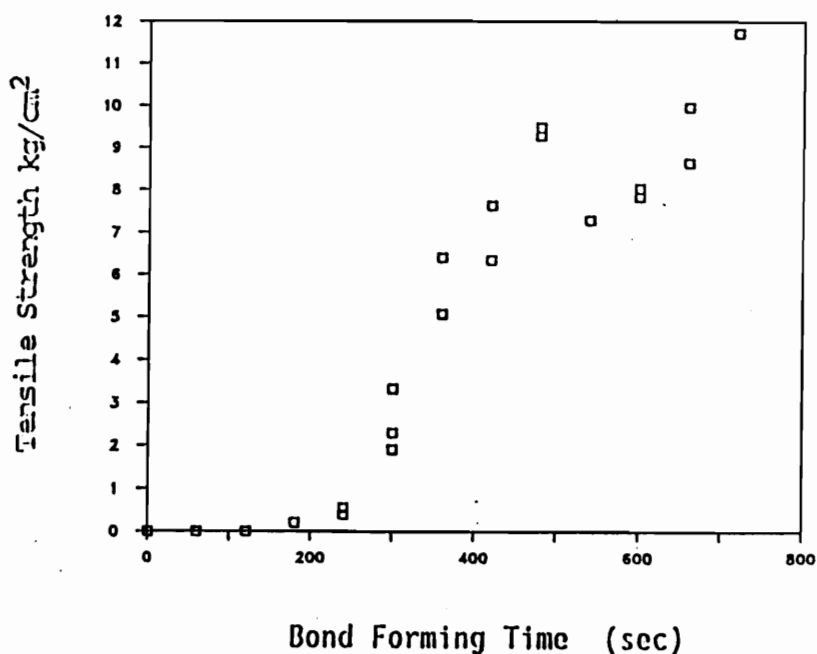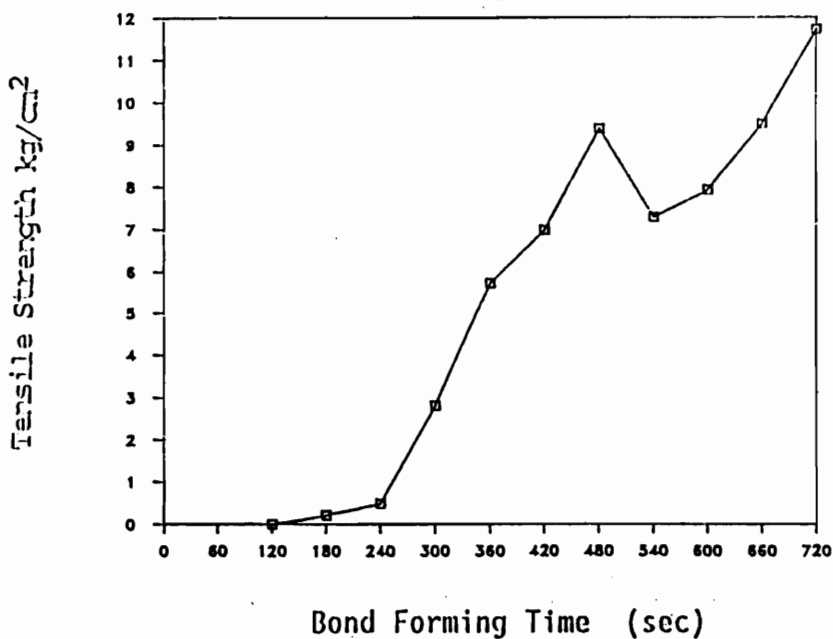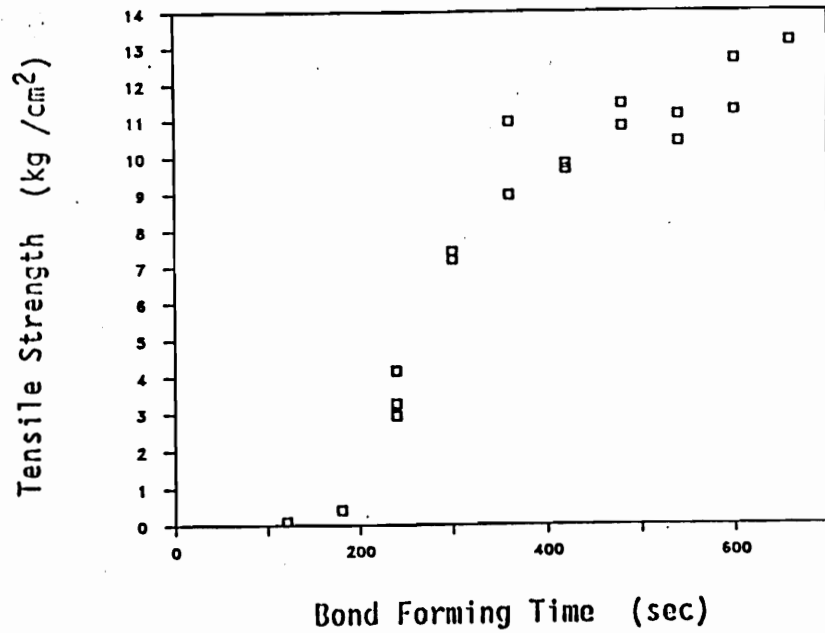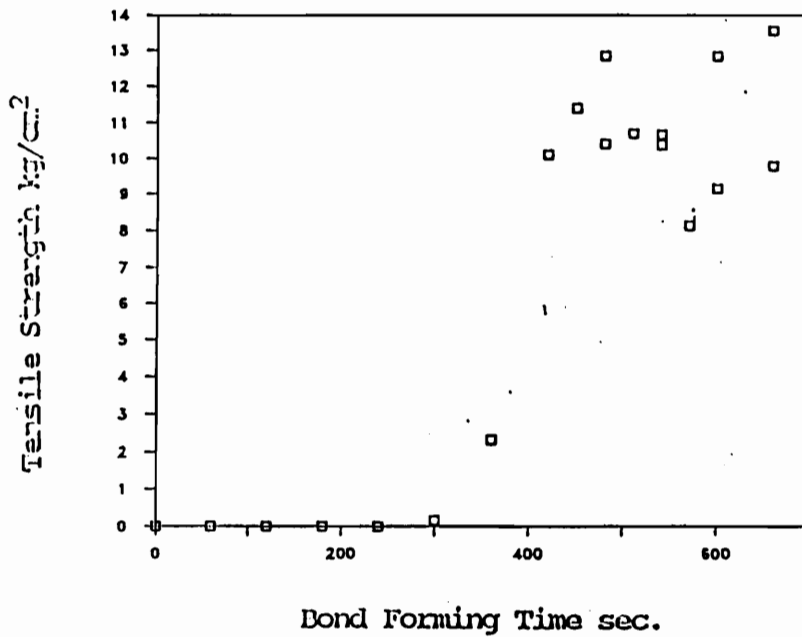
Figure 3-31. Bond strength values for different forming times at constant forming temperature of 115 °C and moisture content of 4 %.
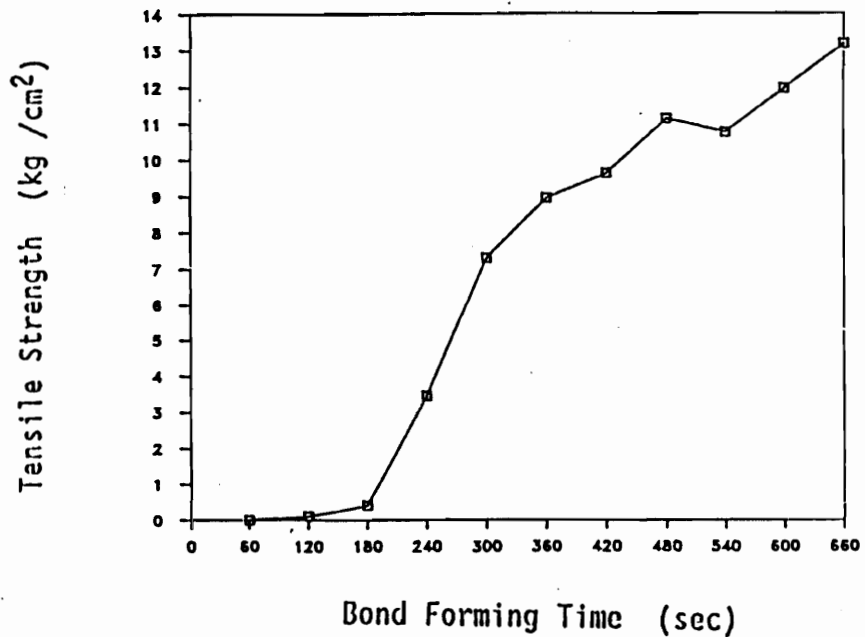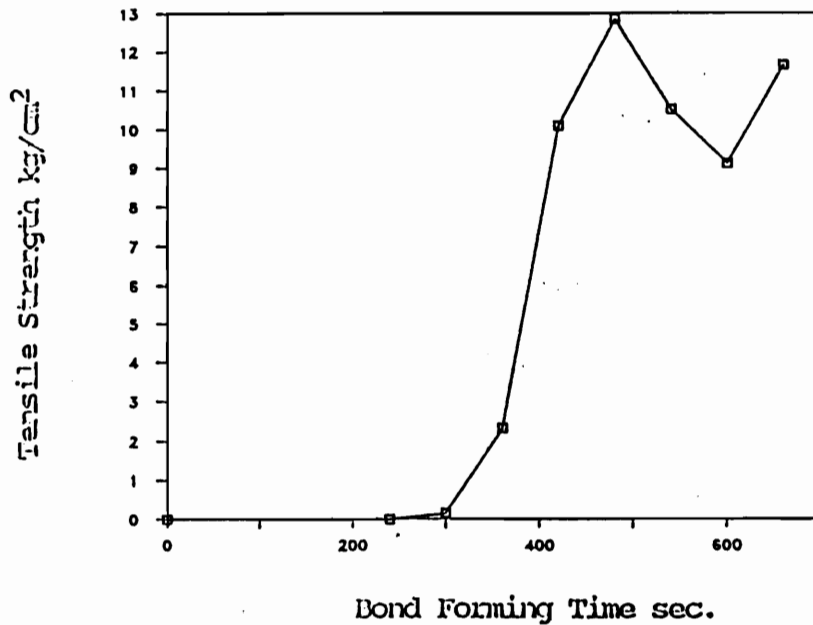

Figure 3-32. Averaged bond strength values versus bond formation time measured at 115 °C temperature and 4 % moisture content.

CHAPTER lV

RESULTS AND DISCUSSION

The characteristics of a typical bond strength development curve will be considered first in section 4.1. Sections 4.2 and 4.3 will concern the effects of temperature, and the combined effects of moisture content and temperature respectively. A brief and preliminary discussion of fracture surfaces and their relationship to bond strength development is included in section 4.4.

4.1. A typical bond strength development curve

Figure 4-1 shows a typical set of bond strength values for a forming temperature of 115 $^{\circ}C$ and moisture content of 10%. Superimposed on this is the corresponding time versus temperature curve measured for the glueline.

Clearly, the interpretation of this data would be simplified if the bond reached the required test temperature instantaneously. Time was, however, required for heat to be transferred to the glueline, and this delay effected rates of bond strength development in the early stages of each test. Referring to Figure 4-1. for 115 $^{\circ}C$ suggests that bonding rates measured during the first 30 seconds will be complicated by changing (unsteady-state) temperatures. It would, in future work, be feasible to use iterative techniques to correct for these effects, though in the present discussion these portions of the curves will not be included in numerical analysis.
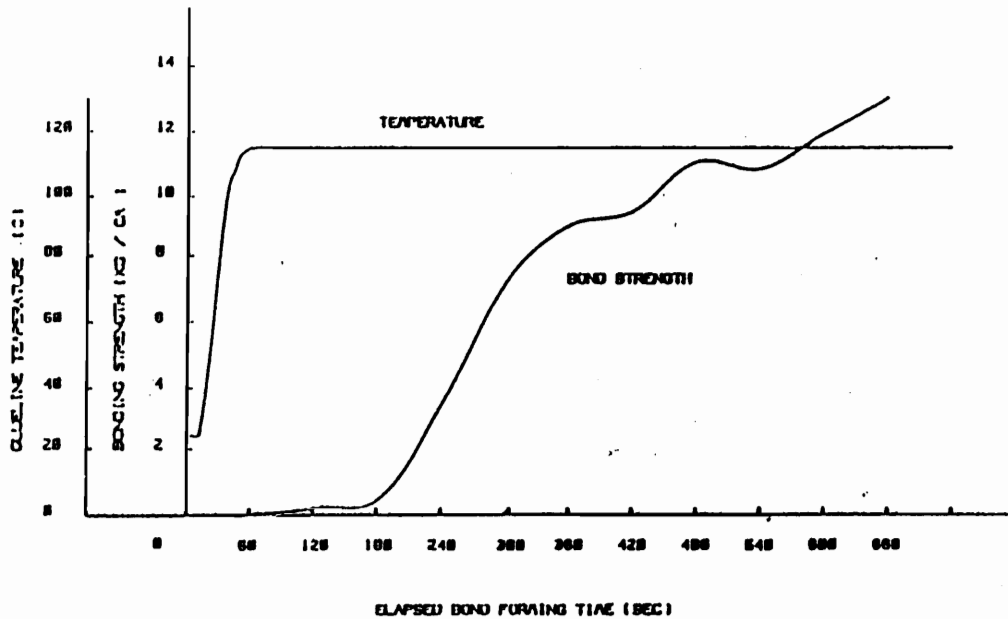
Figure 4-1. A typical set of bond strength values (at 115°C and 10% of moisture content) with glueline temperature curve superimposed

A well defined rate of strength development occurred once steady-state temperatures were reached. Subsequently, however, the rates tended to reduce and become erratic before a secondary well defined period began. This phenomenon has been observed by other researchers, but a great deal of difference in the stage at which each transition occurs is evident. Curves from different sources are combined with one from the present work in Figure 4-2 to enable quantitative comparisons to be made.
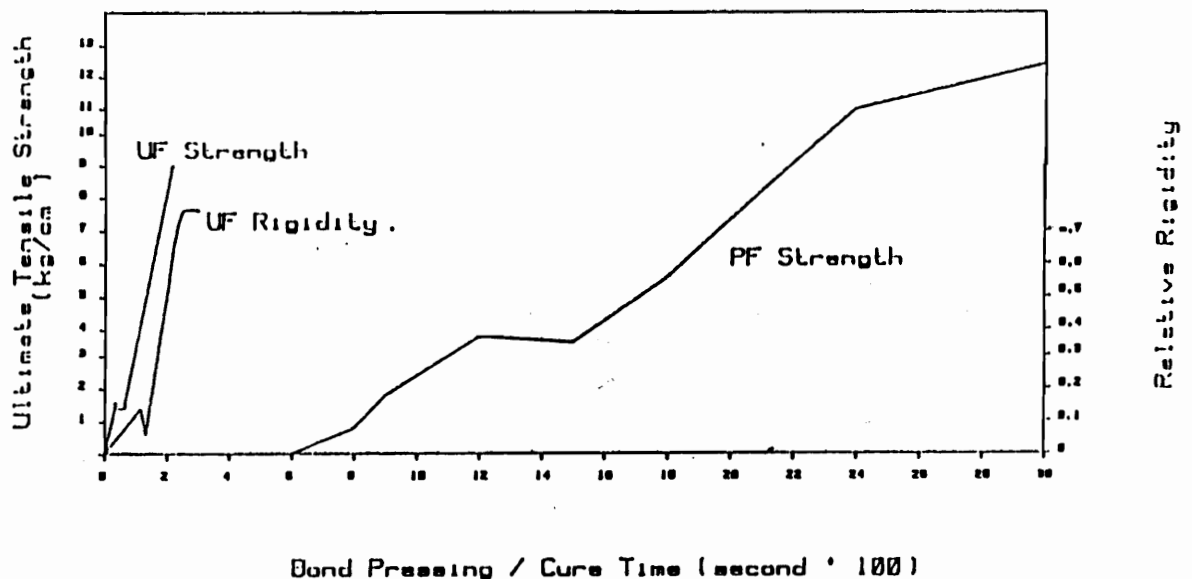
Figure 4-2. A comparison of data derived from different techniques. UF is from Humphrey and Bolton (1978), TBA (UF) is from Wenger (1987), and PF is from the current tests with powdered PF adhesive. These curves are for adhesive cured at 90 °C

Before going on to discuss to shape of this curve, data for all temperatures will be presented.

4.2. The influence of temperature on bond formation

The influence of temperature on the development of bond strength was significant, especially in the initial stages of formation. The higher the temperature, the faster the adhesive cured and the faster the bond developed strength. This is demonstrated in Figure 4-3 showing curves for the range of temperatures tested (in this case, all at 10% moisture content).
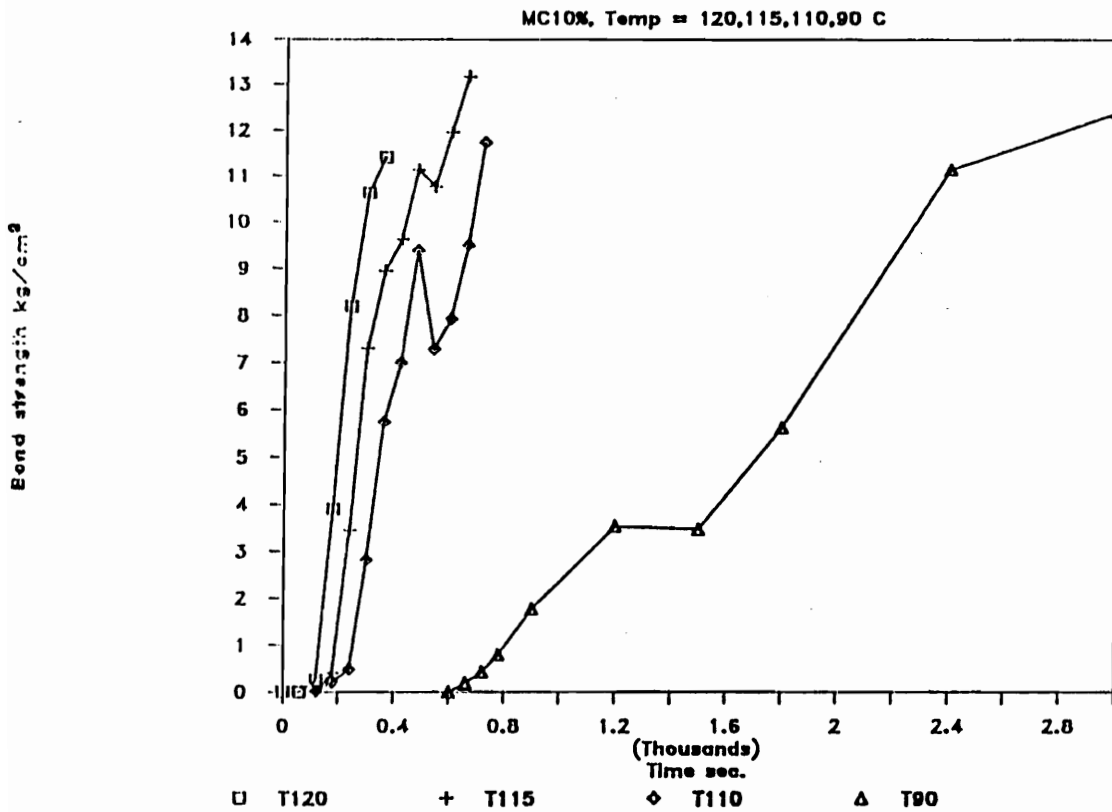
Figure.4-3. The development of bond strength at a range of forming
temperatures but constant moisture content (10% in this
case)

When the other pressing factors are held constant, bond strength

development is only a function of temperature and formation time.

$$S = f (T,t)$$

Where: S = accumulated strength (kg/cm^2)
T = forming temperature (^{O}C)
t = forming time (sec)

The principle of equivalence between temperature and time could

be used here to describe bonding kinetics. This concept of equivalence

combined with the principle of superposition has already been demonstrated by Humphrey and Bolton (1979,1985) to have potential for predicting the development of strength under changing temperature conditions. This concept will be developed further when attempting to use relationships developed here for modelling purposes under the unsteady temperature and moisture conditions that occur in composites during pressing.

Numerical analysis of selected parts of the curves:

Even allowing for the fact that time was needed for the bonds to reach target temperature, it is clear from Figure 4-1. that there is a real delay in the onset of bonding. This portion of the curves has been termed 'stage A' below when considering causes for the behaviour. The delay appears to be inversely related to temperature. To accurately numerically quantify this relationship will require the development of iterative methods to compensate for the changing temperature during the initial stages of formation. In the absence of sufficient data for such an approach to be justified at this stage, an approximate indication can be derived by assuming that no bonding processes occur until the set temperature for each test is reached. The inaccuracy incurred by this assumption is not likely to be very limiting since heating times were small compared to delay periods.

Figure 4-4. below shows how the apparent duration of these delays varies with temperature.

TIME sec.
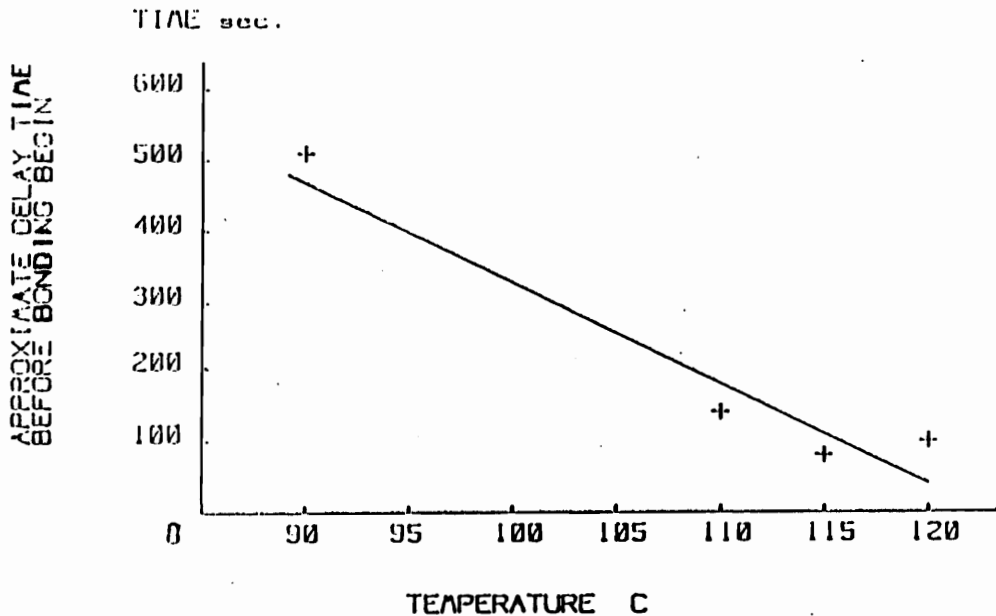
Figure 4-4. Approximate times delay with the different bond forming temperatures

Inclusion of this delay in any models for prediction of bonding in composites will be necessary.

It is clear from Figure 4-3. that temperature increases the rate of bond strength development. The most simple way to analyze these parts of the curves is to linearly regress strength against time for each temperature. Clearly, the initial portions of each curve (before bonding commences) should not be included in such regression. Furthermore, the remainder of each curve consists of different parts. Rather than regressing through all of the points, it would therefore be more valid to consider the effect of temperature on these specific characteristics of the curves separately. The gradients of the portions

important during modeling of hot pressing composites and this is therefore the part of the curves analyzed here. Figure 4-5. shows the derived regression lines which have been offset in the time axis by the delays inferred above.
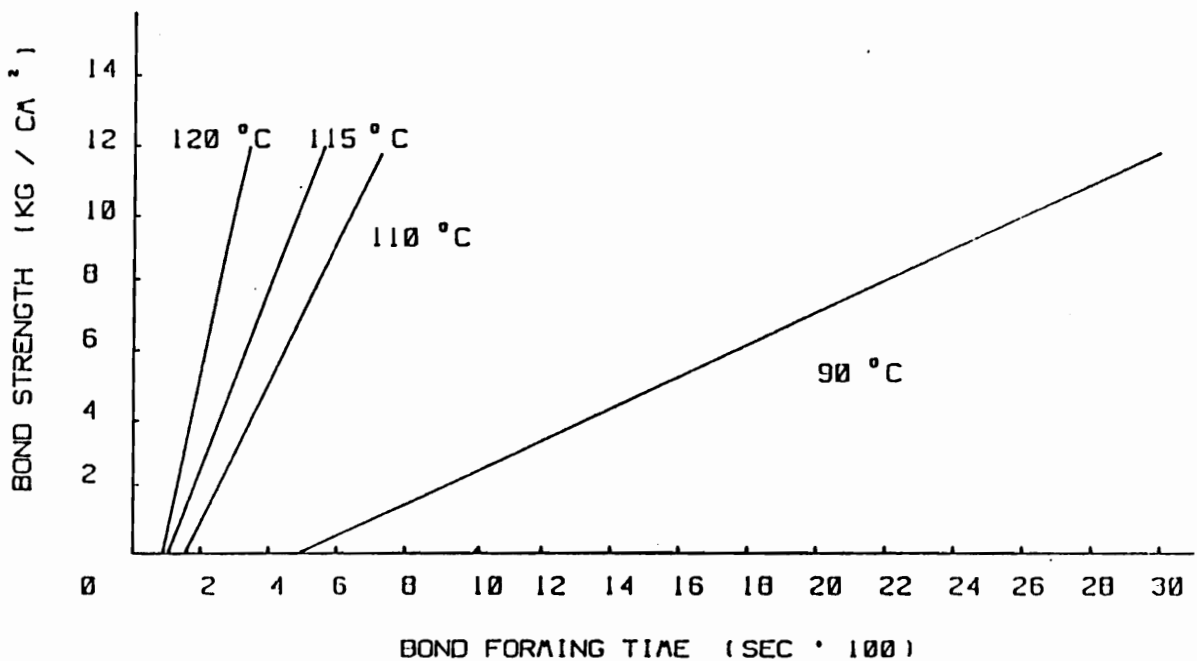
Figure 4-5. Regressed bonding curves with bonding delays included

Figure 4-6. relates temperature to these rates of bonding.
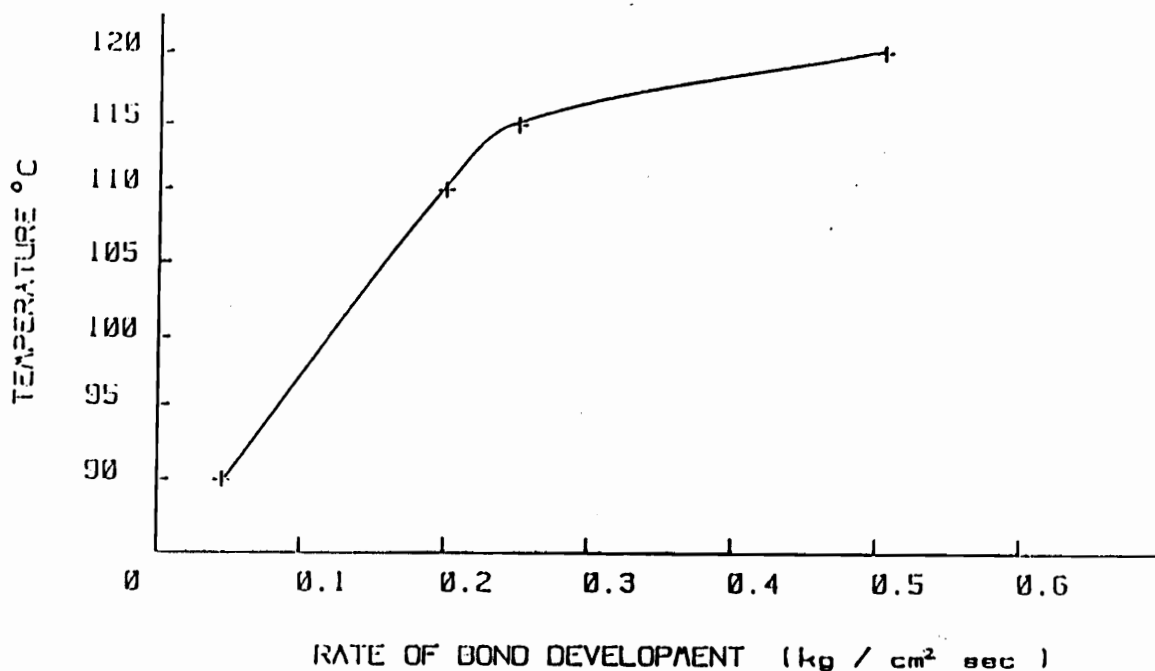
Figure 4-6. The effects of temperature on the rate of bond strength development

An Arrheniaus plot (Ln. rate versus 1/absolute temperature) enables an activation energy value to be derived. Such a plot for the regressed lines of Figure 4-5 have been used to derive the Arrheniaus plot shown as Figure 4-7. An activation energy value of 83 kJ mol^{-1} has been derived by regression.

A similar approach could be taken to derive activation energy values for the other two parts of the curves. These are not, however, well enough defined to justify their calculation at this stage.
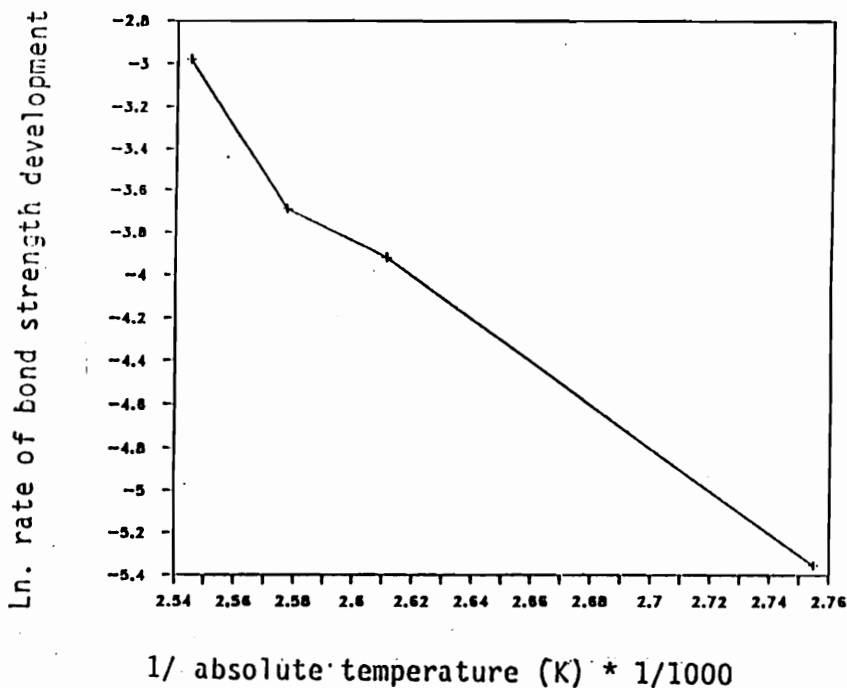
Figure 4-7.   Arrheniaus plot of bond development at the early
stages of cure

Possible causes of discontinuities in strength development:

The reason for the non-linearity of bond strength development with time is not readily apparent. It may be that during bond formation, the powdered adhesive melts, spreads, and flows into the porous wood. At the same time, polymerization leads to changes of the adhesive from linear molecules to a three dimensional network. This is a continuous process as the adhesive changes from powder or liquid (in the case liquid systems) to the fully cured state. The viscosity and surface tension of the adhesive changes during this process and this effects flow and spread within the glueline during pressing.

The strength development curve may be divided into four parts which are identified as stages A, B, C and D in Figure 4-8.
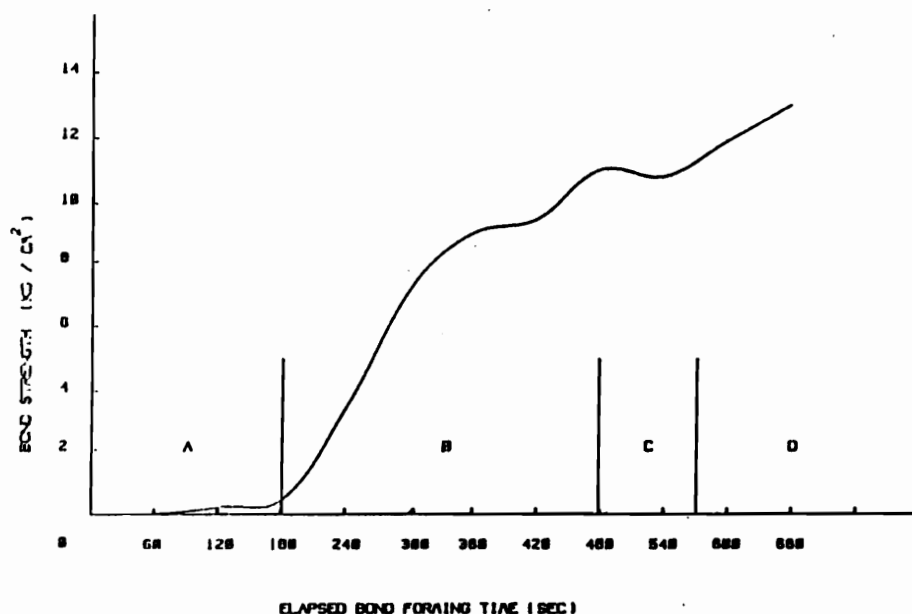
Figure 4-8. Four stages identified for the analysis of bond strength development

Stage "A" may correspond to adhesive melting and spreading described above. Bond strength is negligible and only the result of viscous restraint.

Stage "B" may be the result of condensation to form larger molecules and small networks begin to form. At this stage, the adhesive may have reached its maximum dispersion in the surrounding wood. Bond strength increases rapidly and almost linearly with time. The viscosity of the adhesive is likely to increase rapidly but it still may be regarded as a fluid.

The onset of stage "C" corresponds to a reduction in strength development rate. The cause of this discontinuity is not known. It is highly pronounced (more than displayed here) when similar tests are

conducted on urea formaldehyde to wood systems (Humphrey and Bolton,1979). It may be that the adhesive begins to form a three-dimensional network where the initial or temporary molecular bonds were broken and rearranged. The viscosity of the adhesive may change relatively little during this stage.

Stage "D" of adhesive curing is well defined though somewhat slower than that during stage "B". Clearly, the adhesive has reached a high level of cross-linking. Reference to fracture surfaces does, however, suggest that at elevated temperature the polymer is thermoplastic. Photographs presented in Chapter V (Figure 5-?) show the formation of whiskers of polymer extruded or drawn from the surface. This is combined with an increase in the removal of wood fibers from the fracture surfaces as the cohesive strength of the wood is approached.

4.3. The influence of both temperature and moisture content on
      the development of bond strength

The combined influences of both moisture content and temperature on the development of bond strength is also significant but less clearly defined. Figure 4-9. shows the development of bond strength under different moisture conditions (4, 10, and 16%) and temperatures of 115 $^\circ$C and 110 $^\circ$C.

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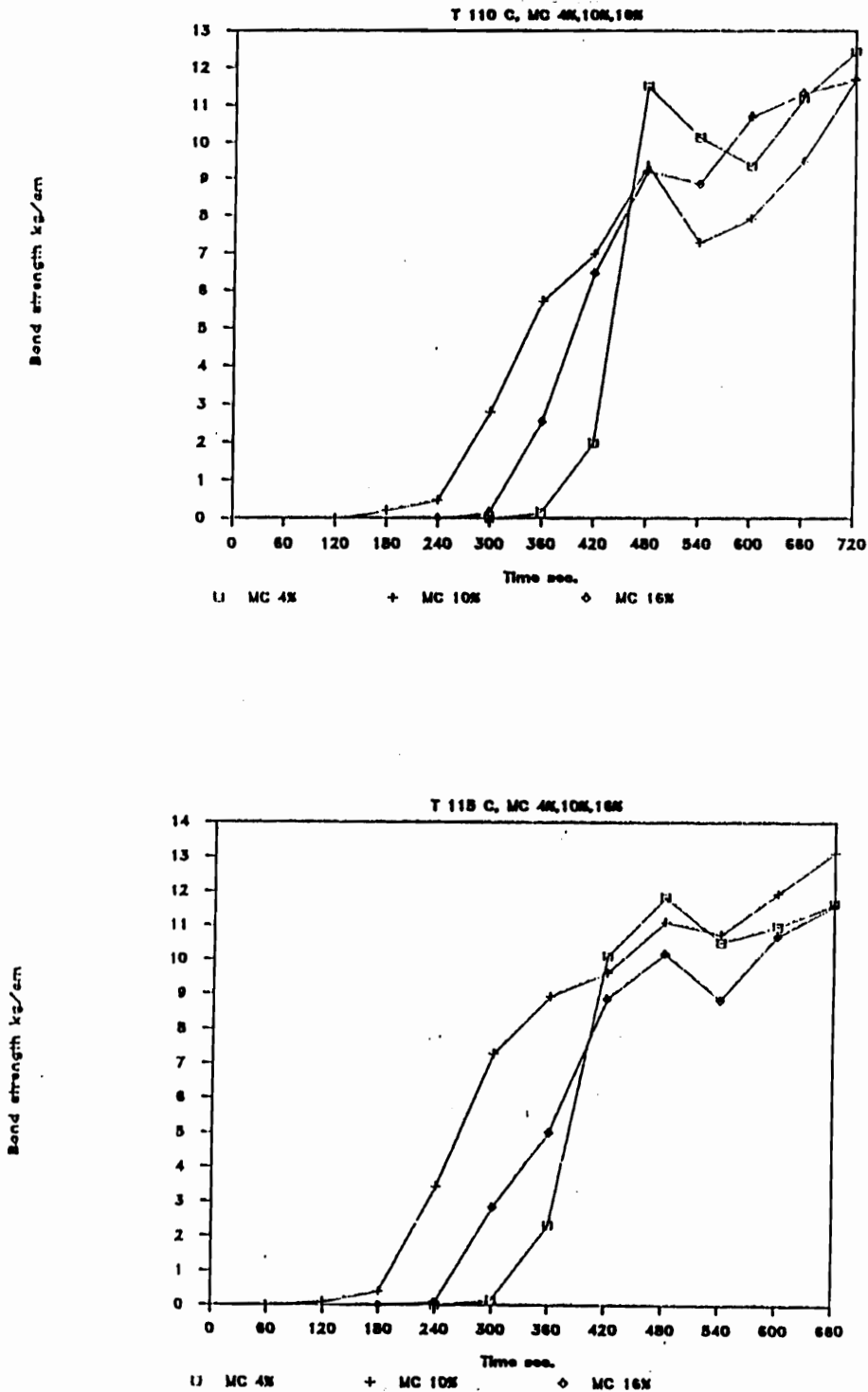
Figure 4-9. Development of bond strength under two forming
temperatures and three moisture conditions (above is
110 °C, the other is 115 °C)

At both temperatures, moisture content effected the early stages of bond formation most clearly. The duration of the delay before significant strength development occurred (stage "A") was shortest at the 10% moisture level, with values above this (16%) leading to moderately greater times, and lower values (4%) being very much extended. Clearly this suggests there is a range of moisture values which are optimum for the rapid initiation of curve. Figure 4-10. below shows the influence of moisture content on the initial period (A) for both 110 $^{\circ}$C and 115 $^{\circ}$C.
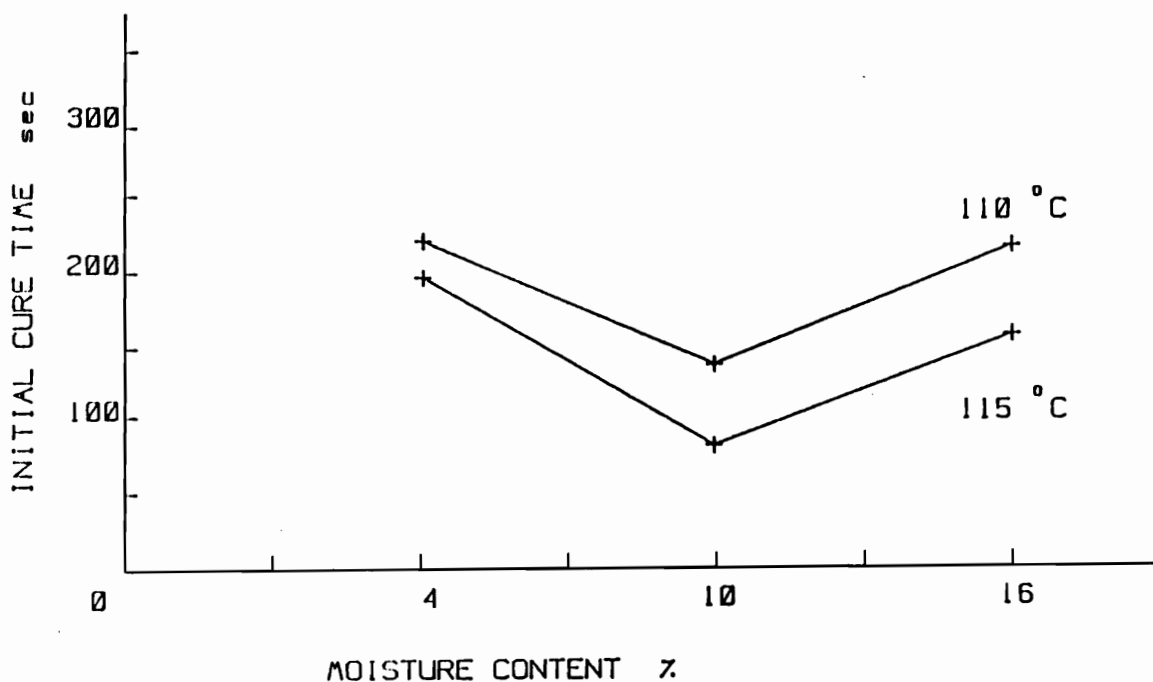
Figure 4-10. The influence of moisture content on the duration of stage "A"

It is possible that this intermediate quantity of moisture helped the powder adhesive to liquidize, spread and flow over the wood

surface. Higher moisture values may have reduced the availability of bonding sites within the wood. It may also have reduced the reactivity of the adhesive and possibly reduced the viscosity of the melted adhesive to values which led to inappropriate adhesive dispersal in the bonding zone. At the lowest moisture level (4% MC), greater time may have been needed to melt or dissolve the adhesive before bonding could commence.

The effect of temperature and moisture, together, on the delay time is represented graphically as Figure 4-11. Rather surprisingly, the influence of temperature appears to be greatest at the (10%) moisture level and least at the 4% moisture level. One would expect melting of adhesive in the presence of low levels of water (4%) to be highly dependent on temperature.
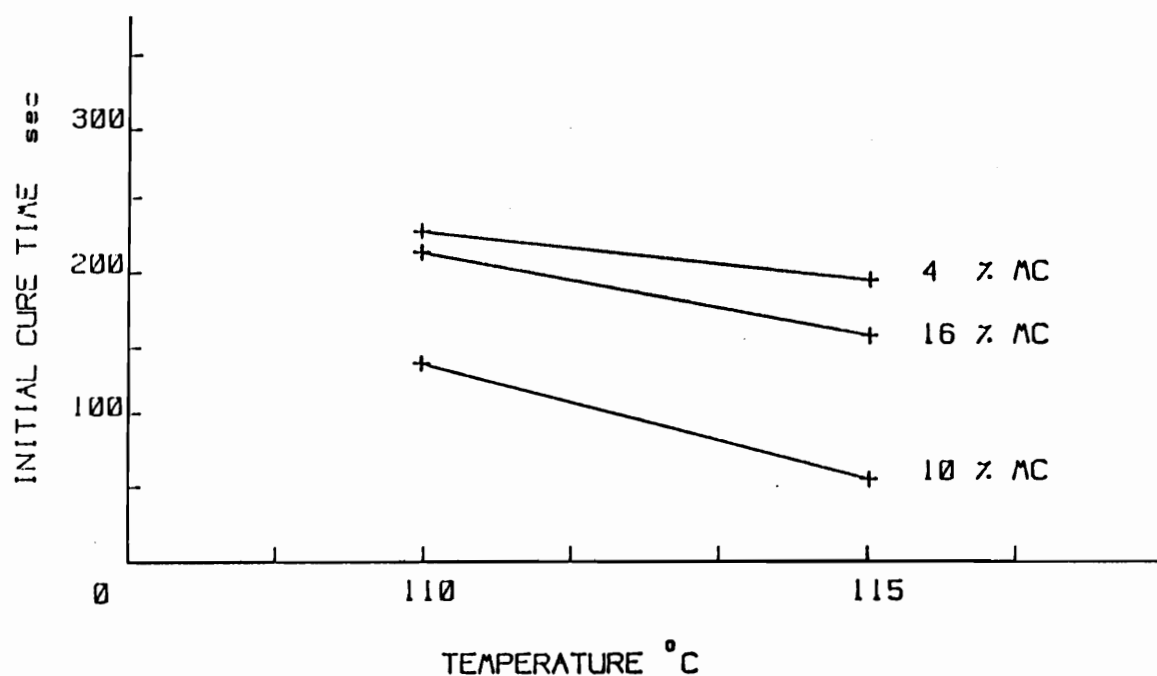
Figure 4-11. Initial cure time at different temperature and moisture conditions

Once significant bond strength development begins (stage "B"), bonds formed under all conditions exhibited a well defined rate of strength development. Interestingly, once initiated, the driest bonds (4%) developed strength most rapidly and by the end of stage "B" had reached strength values similar to those formed at 10% moisture content. Numerical analysis of these curves is not considered justified in light of their complexity and our low levels of replication. The interaction of temperature, moisture content and pressing time are, however, clearly evident in Figure 4-9.

4.4. Preliminary description of fracture surfaces

In addition to the main focus of this study (bond strength kinetics), it has been possible to relate mechanisms of failure in test bonds to the conditions under which they were formed. What follows is a very brief outline of the way that this testing method may, in future work, be used to shed light on failure mechanisms.

These preliminary studies have related the characteristics of fracture surfaces to accumulated bond strength. Following testing of selected bonds, the exposed surfaces have been observed with the microscope and photographs were taken to demonstrate the more obvious features.

For the purposes of this preliminary discussion, a single set of forming conditions has been selected. These were a temperature of 120 $^{\circ}$C and moisture content of 10%. Clearly, an indication of progressive changes in the mechanisms of stress distribution that occur in the bond can be gained by examining fracture surfaces derived from tests at a

range of stages in the curing cycle. Figures 4-13, 4-14, and 4-15 show cross sectional views of wood disks - looking parallel to the fracture surfaces. Clearly, there is a progressive change in the rheological properties of the adhesive and its interaction at the wood-polymer interface.

The bond strength development curve for 120 °C and 10% moisture content is reproduced below as Figure 4-12 and the locations of the fracture surfaces for Figure 4-13 to 4-15 are superimposed.
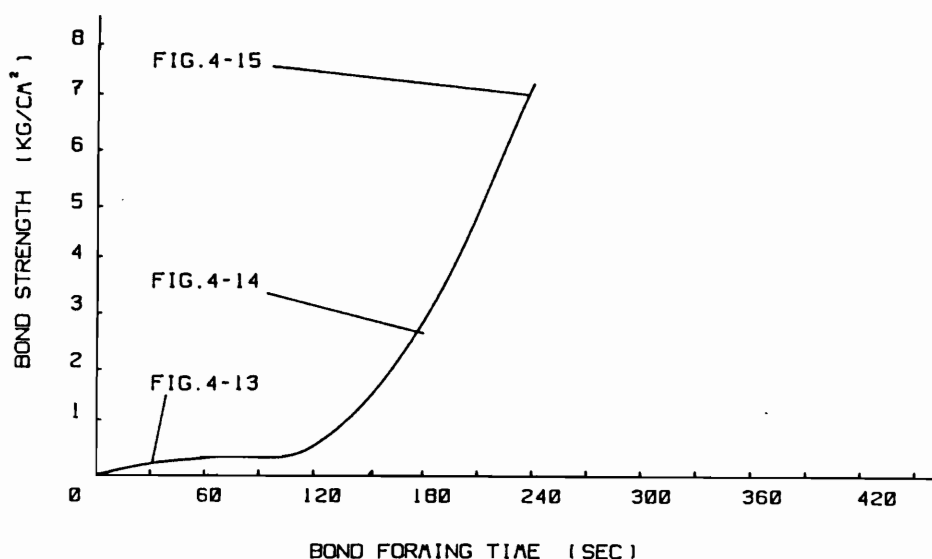
Figure 4-12. The three stages in the bond strength development curve for which fracture surfaces are presented

At early stages of bonding (Figure 4-13) the adhesive appeared to have been fused from a powder to a viscous liquid. Many long fine

adhesive whiskers were pulled from the surface during bond failure. Such bonds exhibited strengths of 0.5 to 0.7 kg/cm^2. No wood failure was evident and the strength appeared to depend on the viscosity of the adhesive.

Figure 4-13. Failure surface of tension test at 30 sec. press time, 120 $^\circ$C press temperature, 10% moisture content. There were long, fine adhesive fibers on the surface, suggesting cohesive within the failure adhesive. The tension strength was 0.31 kg/cm^2

As polymerization progressed, the viscosity of the hot adhesive appeared to increase. After 180 seconds of bond formations, strengths had reached 2.5 to 4.5 kg/cm^2 and the associated surface is shown below as Figure 4-14.
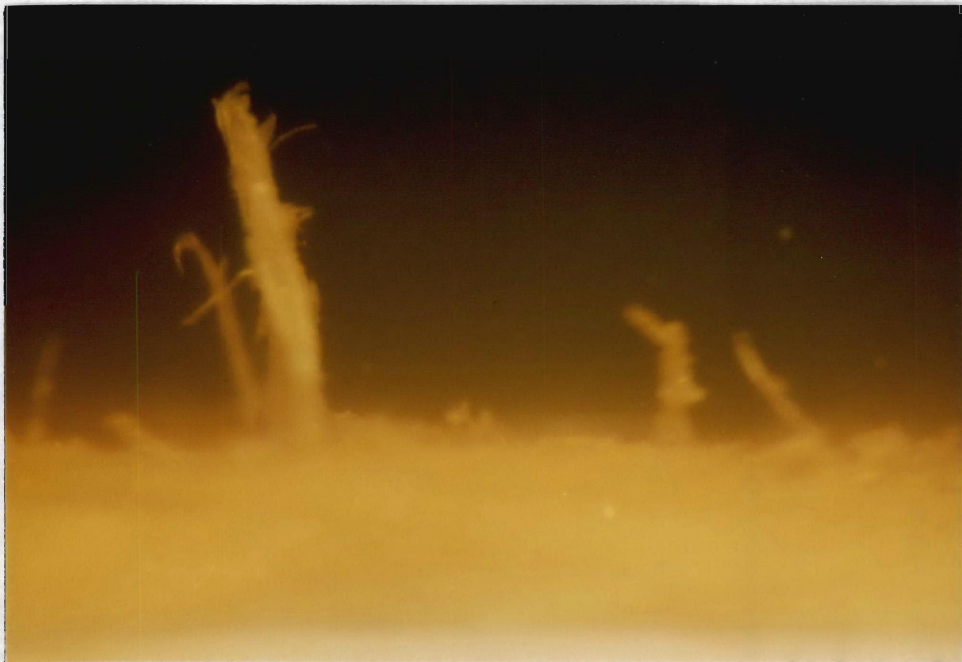
Figure 4-14. Failure surface for a bond formed for 180 sec., 120 $^{\circ}$C press temperature, 10% moisture content. The failure mostly occured at the interface though some wood fibers have been broken. The tension strength was 2.594 kg/cm^2

Some failure appeared to occur near the adhesive / wood interface, though there were also come short and quite strong adhesive whiskers distributed non-continuously over the surface. One might expect measured strengths at this and preceeding stages to be highly dependent on the rate of loading since viscous flow is involved.

Fully cured bonds exhibited a high degree of wood failure and some interfacial delamination. (Figure 4-15. below). No extrusion of the adhesive (viscous flow) was detected.

Figure 4-15. Failure surface of a bond formed for 240 sec., 120 $^{\circ}$C press temperature, 10 % moisture content. The failure surface displays wood failure. The tension strength was 7.129 kg/cm^2

Preliminary analysis of bonds formed at different temperatures (110 ^oC) suggest that, though bonding rates clearly differ, fracture surfaces were very similar at the same bond strength values. One would not, however, expect this similarity to hold for large difference in temperature and moisture content. Changes in viscosity of the adhesive would, most likely, effect the relative importance of adhesive bonding versus cohesive deformation both in the wood and in the polymer.

Clearly, this data is highly preliminary and is only included to demonstrate the concept of relating the characteristics of failure surfaces to forming conditions. The usefulness of this approach as a tool in future work in discussed in the concluding chapter to follow.

CHAPTER V

CONCLUSIONS AND FUTURE RESEARCH

5.1. Conclusions of current research

The following are the essential conclusions of the current work:

1. A method has been successfully developed to form test adhesive bonds under controlled conditions of temperature, moisture content and time.

2. A finite though small delay occurs before steady conditions are reached for each bond being formed.

3. Powdered adhesive was tested in tension perpendicular to the bond after forming at temperatures from 90 to 120 ^{o}C and from 4% to 16% moisture content.

4. Bonding under all conditions consists of a number of stages. These include: initial delay; rapid rise in strength; decreased bonding rate; and finally, rapid secondary rise.

5. Temperature had a clear effect on all stages. An activation energy of 83 kJ / mole was measured for the initial rapid stage.

6. Moisture content effects were also evident though more complex. For each stage, an optimum moisture content appeared to exist.

7. Fracture surface may be related to stages in the polymerization of the adhesive and associated changes in viscosity.

5.2. Future research

Future work following on from that described here may include the following:

1. Improvements in the levels of replication are necessary to enable reliable correlations to be derived for the combined effects of moisture content and temperature for all stages of cure. A wider range of moisture and temperature conditions should also be investigated.

2. The derived data will be used to predict (model) adhesion within wood based composites under the changing conditions of moisture content and temperature already known from models. This will involves numerical methods of simulation.

3. The method may be used as a tool to quantitatively investigate the effects of a wide range of bonding conditions (substrate, adhesive, surface conditions, and forming condition).

4. Microscopic analysis of fracture surface may enable failure mechanisms to be linked to bond performance and forming conditions.

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APPENDIX

APPENDIX

RAW DATA AND STATISTICAL REDUCTION

Data reduction:

Bonds were formed under a total of four temperature and three moisture content values. Two or three replications for each bonding condition (moisture content, temperature and time) were measured. Basic strength data are presented here for all tests conducted.

MC = 10 %, T = 120 °C		MC = 10 %, T = 90 °C	
Time (sec)	Bond strength (kg/cm^2)	Time (sec)	Bond strength (kg/cm^2)
0		600	0
60	0	660	0.1988
120	0.2002	720	0.4272
120	0.4160	780	0.7984
150	0.7987	900	1.1042
180	4.5102	900	2.4539
180	3.2828	1200	2.6100
240	8.0060	1200	4.4040
240	7.1290	1200	3.6192
240	9.4356	1500	3.5089
300	8.8070	1500	3.1448
300	13.2119	1500	3.7945
300	8.0182	1800	5.4049
		1800	5.8550
		2400	11.1444
		3000	12.4055

MC = 10 %, T = 115 °C

Time (sec)	Bond strength (kg/cm^2)
0	
60	0
120	0.1001
180	0.4080
180	0.4150
240	3.2687
240	2.9395
240	4.1610
300	7.4067
300	7.2024
360	8.9551
360	8.9620
420	9.8062
420	9.6627
480	11.4416
480	10.8080
540	11.1283
540	10.3881
600	12.6806
600	11.2449
660	13.1702

MC = 10 %, T = 110 °C

Time (sec)	Bond strength (kg/cm^2)
0	
60	
120	0
180	0.2110
240	0.4120
240	0.5604
300	2.2987
300	1.9104
300	3.3340
360	6.4058
360	5.0686
420	6.3433
420	7.6430
480	9.2802
480	9.4836
540	7.2871
600	7.8384
600	8.0292
660	8.8296
660	9.9607
720	11.7225

MC = 16 %, T = 115 °C

Time (sec)	Bond strength (kg/cm^2)
0	
60	
120	
180	0
240	0.0813
300	2.8438
360	5.0327
420	8.8657
450	11.1726
480	10.2995
480	10.0760
510	8.8079
540	8.3385
540	8.1611
570	10.0711
600	9.1335
600	11.6709
660	11.6055

MC = 16 %, T = 110 °C

Time (sec)	Bond strength (kg/cm^2)
0	
60	
120	
180	
240	0
300	0.1601
360	2.5546
420	5.1238
420	5.8276
450	8.4691
480	10.9500
510	6.4878
540	9.9251
570	10.2092
600	9.1335
600	11.6709
630	11.8878
660	10.0632
660	12.0813
720	11.7093

MC = 4 %, T = 115 ^{O}C   MC = 4 %, T = 110 ^{O}C

Time (sec)	Bond strength (kg/cm^2)	Time (sec)	Bond strength (kg/cm^2)
0		0	
60		60	
120		120	
180		180	
240	0	240	
300	0.1610	300	0
360	2.3426	360	0.1606
360	2.8006	420	2.9195
420	10.1091	420	1.0377
450	11.4103	450	10.9214
480	12.8476	450	11.1079
480	10.9667	480	12.3157
510	10.7032	510	11.7566
540	10.3810	540	11.3382
540	10.6718	570	8.5564
570	8.1301	570	8.9667
600	9.1367	600	10.5461
600	12.8319	600	10.4722
660	9.7816	660	11.2110
660	13.5461	720	12.7741
		720	12.1079

In addition, a small number of tests were conducted using a different type of powdered PF adhesive. These were formed at 120 ^{O}C and 10% moisture content. These results were used only for studies of bonding surfaces. They were not included in numerical analysis

Time (sec)	Bond strength (kg/cm^2)
0	0
30	0.2000
30	0.3120
60	0.4060
60	0.6010
120	1.6010
120	2.0300
180	4.5680
180	2.5640
240	7.1290
240	5.8720
300	7.3090
300	6.4040
360	9.0060
360	10.7600

Statistical methods:

Separate regression equations relating accumulated bond strength
with time were required for each of the temperature and moisture
content values used.

Several regression models were used to determine the best fit for
the distribution of the measured bond strength values during the period
of initial stength development (stage B). These included logarithmic
and linear functions, and linear regression was found to be most
appropriate.

Temperature (^{O}C)	MC (%)	R	Regression model
90	10	0.9478	$Y = -2.4279 + .004736X$
110	10	0.9263	$Y = -2.7699 + .019956X$
115	10	0.9511	$Y = -1.9711 + .025078X$
120	10	0.9249	$Y = -4.9814 + .050861X$
110	4	0.7475	$Y = -6.3302 + .028372X$
115	4	0.8028	$Y = -5.6924 + .029201X$
110	16	0.9151	$Y = -6.0083 + .027253X$
115	16	0.8960	$Y = -3.8887 + .025179X$

The initial bond forming time and the rate of bond strength development were expressed for each of the conditions as follows:

Forming condition (MC / T)	Initial time (stage A)	Rate of bond forming (stage B)
(% / °C)	(sec)	(kg / cm^2 * sec)
10 / 90	512.7559	.004736
10 / 110	138.8056	.019956
10 / 115	78.5984	.025078
10 / 120	97.9417	.050861
4 / 110	223.1125	.028372
4 / 115	194.9387	.029201
16 / 110	220.4612	.027253
16 / 115	154.4412	.025179

Regression results and related data:
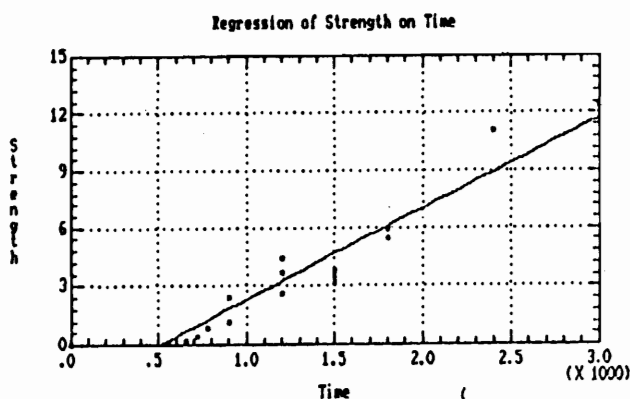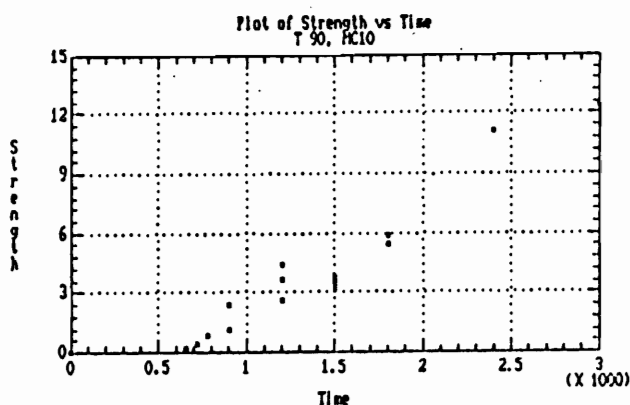
Plot of Strength vs Time
T 90, MC10

Regression of Strength on Time

Simple Regression of Strength on Time

Parameter	Estimate	Standard Error	T Value	Prob. Level
Intercept	-2.42794	0.634289	-3.82781	1.84661E-3
Slope	4.73508E-3	4.25872E-4	11.1185	2.47447E-8

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio
Model	174.25957	1	174.25957	123.62175
Error	19.734666	14	1.409619	
Total (Corr.)	193.99424	15		

Correlation Coefficient = 0.947772
Stnd. Error of Est. = 1.18727

Regression analysis on 90 ^{o}C temperature and 10% moisture condition of bond formation
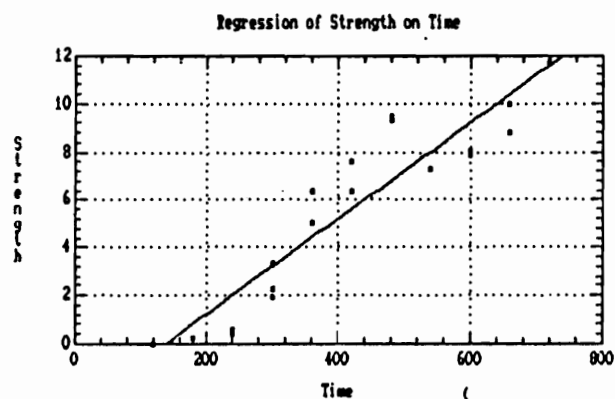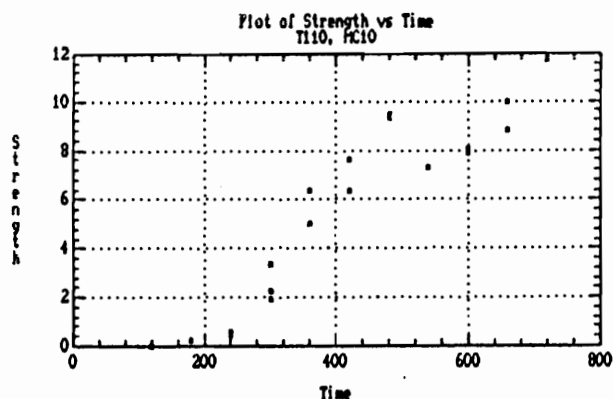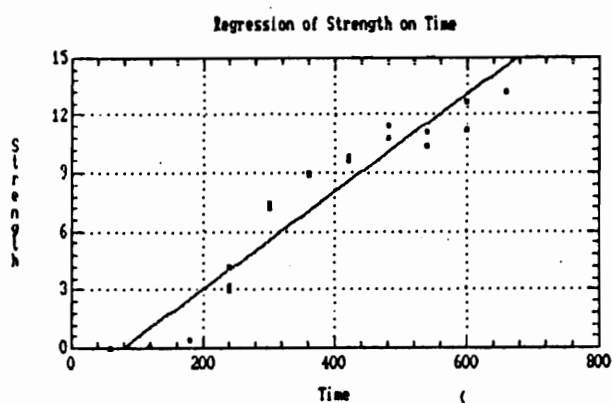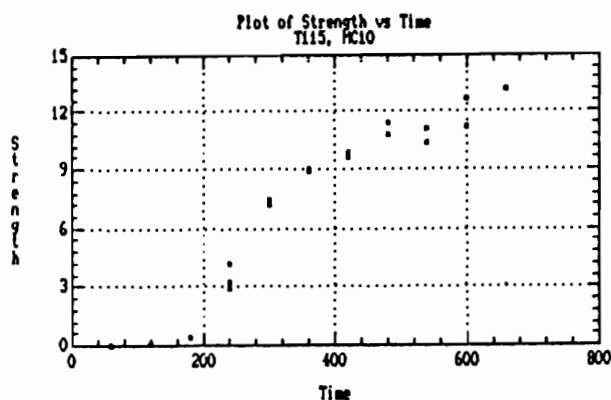
Plot of Strength vs Time
TI10, MC10

Regression of Strength on Time

Simple Regression of Strength on Time

Parameter	Estimate	Standard Error	T Value	Prob. Level
Intercept	-2.76999	0.89286	-3.10238	6.47169E-3
Slope	0.0199559	1.96922E-3	10.1339	1.27352E-8

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio
Model	220.78356	1	220.78356	102.69651
Error	36.547694	17	2.149864	
Total (Corr.)	257.33125	18		

Correlation Coefficient = 0.926269
Stnd. Error of Est. = 1.46624

Regression analysis on 110 °C temperature and 10% moisture condition of bond formation
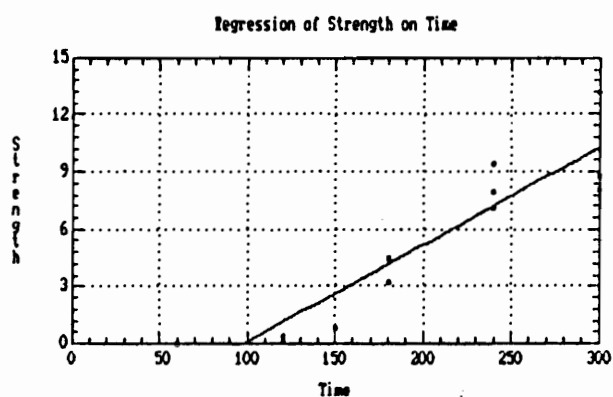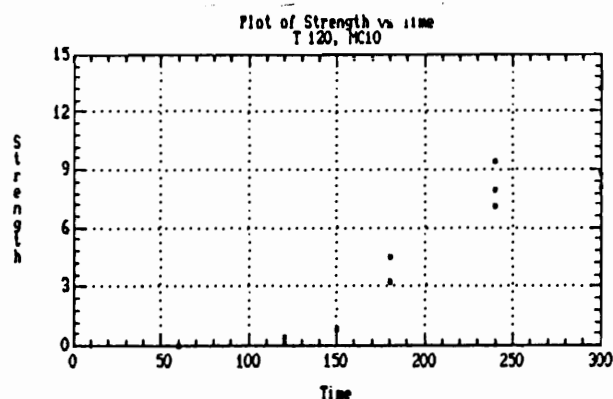
Plot of Strength vs Time
T115, AC10

Regression of Strength on Time

Simple Regression of Strength on Time

Parameter	Estimate	Standard Error	T Value	Prob. Level
Intercept	-1.97109	0.773892	-2.54699	0.0202268
Slope	0.025078	1.92062E-3	13.0573	1.2812E-10

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio
Model	357.26893	1	357.26893	170.49209
Error	37.719290	18	2.095516	
Total (Corr.)	394.98822	19		

Correlation Coefficient = 0.951055
Stnd. Error of Est. = 1.44759

Regression analysis on 115 $^{\circ}C$ temperature and 10% moisture condition of bond formation

Plot of Strength vs Time
T 120, MC10

Regression of Strength on Time

Simple Regression of Strength on Time

Parameter	Estimate	Standard Error	T Value	Prob. Level
Intercept	-4.98144	1.4313	-3.48035	5.91776E-3
Slope	0.0508613	6.61091E-3	7.69353	1.6551E-5

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio
Model	182.18014	1	182.18014	59.19038
Error	30.778672	10	3.077867	
Total (Corr.)	212.95881	11		

Correlation Coefficient = 0.924917
Stnd. Error of Est. = 1.75439

Regression analysis on 120 °C temperature and 10% moisture condition of bond formation

Plot of Strength vs Time
M.16, T110
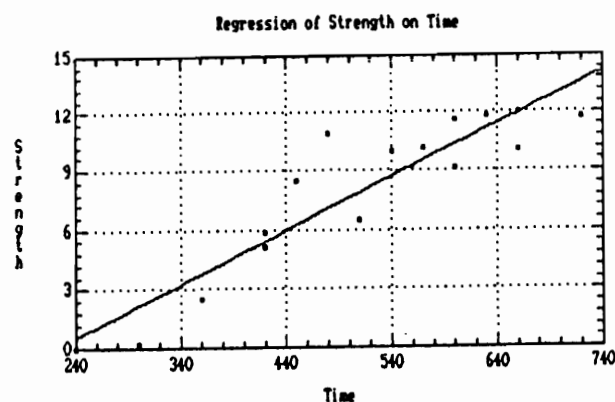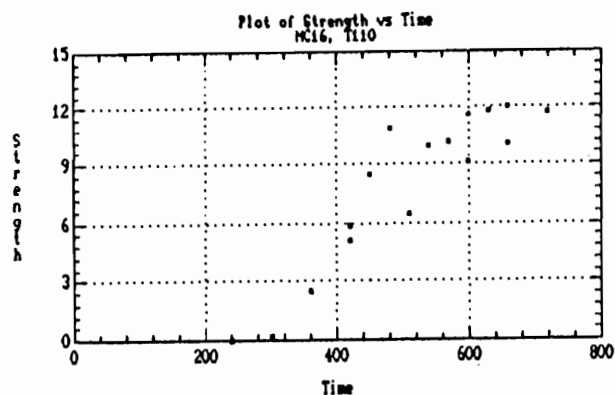

Regression of Strength on Time

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Simple Regression of Strength on Time
                              Standard                T              Prob.
Parameter        Estimate      Error               Value             Level
--------------------------------------------------------------------------
Intercept       -6.00825      1.69215            -3.55066        3.19676E-3
Slope          0.0272531    3.21007E-3            8.48987         6.8106E-7

------------------------------------------------------------------------
                   Analysis of Variance
------------------------------------------------------------------------
Source          Sum of Squares    Df    Mean Square    F-Ratio
Model              211.23285       1     211.23285     72.07795
Error              41.028636      14      2.930617
------------------------------------------------------------------------
Total (Corr.)      252.26148      15

Correlation Coefficient = 0.915072
Stnd. Error of Est. = 1.7119
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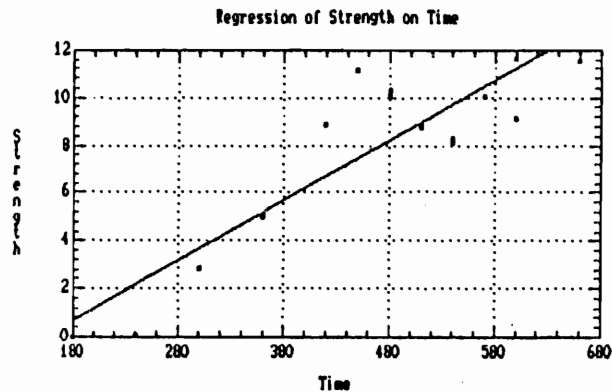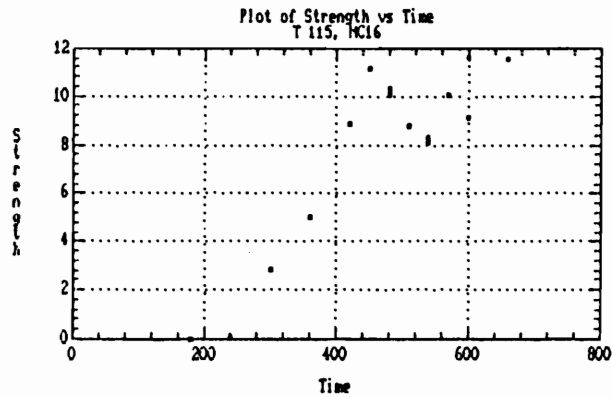
Regression analysis on 110 ^{O}C temperature and 16% moisture condition of bond formation

Plot of Strength vs Time
T 115, HC16

Regression of Strength on Time

Simple Regression of Strength on Time

Parameter	Estimate	Standard Error	T Value	Prob. Level
Intercept	-3.88866	1.66564	-2.33464	0.0362487
Slope	0.0251789	3.46153E-3	7.27394	6.23584E-6

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio
Model	172.08728	1	172.08728	52.91016
Error	42.281763	13	3.252443	
Total (Corr.)	214.36904	14		

Correlation Coefficient = 0.89597
Stnd. Error of Est. = 1.80345

Regression analysis on 115 °C temperature and 16% moisture condition of bond formation

Plot of Strength vs Time
T 110, MC4
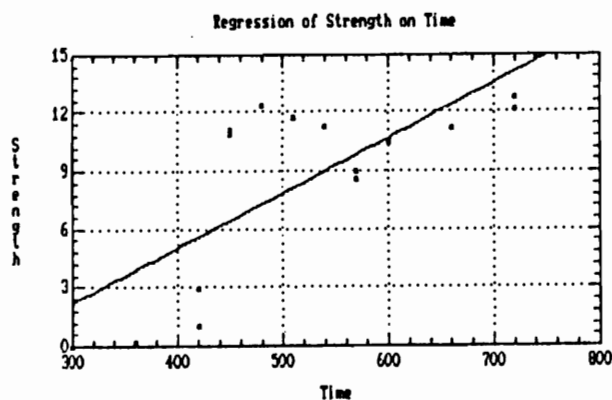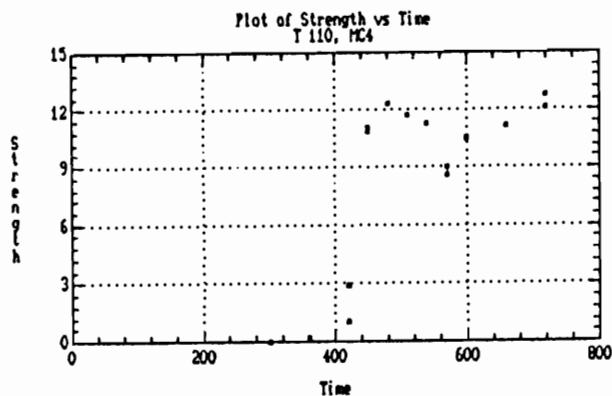

Regression of Strength on Time

Simple Regression of Strength on Time

Parameter	Estimate	Standard Error	T Value	Prob. Level
Intercept	-6.33017	3.61326	-1.75193	0.101651
Slope	0.0283721	6.73751E-3	4.21107	8.71591E-4

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio
Model	179.62567	1	179.62567	17.73309
Error	141.81171	14	10.12941	
Total (Corr.)	321.43738	15		

Correlation Coefficient = 0.747543
Stnd. Error of Est. = 3.18267

Regression analysis on 110 °C temperature and 4% moisture condition of bond formation
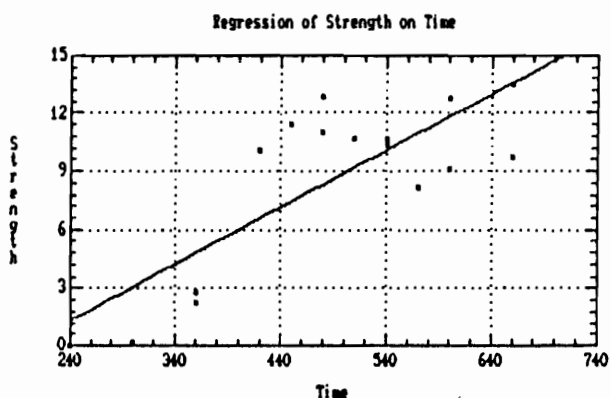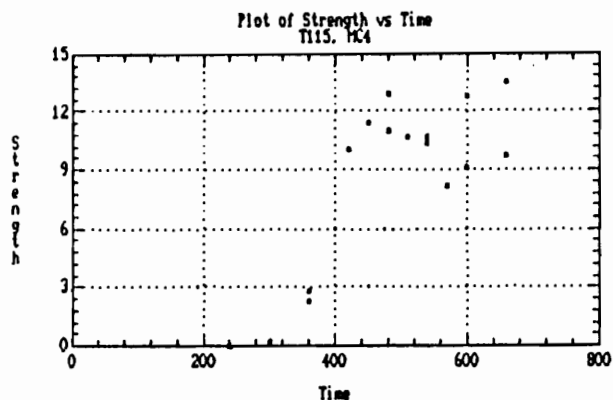
Plot of Strength vs Time
T115, M4

Regression of Strength on Time

Simple Regression of Strength on Time

Parameter	Estimate	Standard Error	T Value	Prob. Level
Intercept	-5.69241	2.90034	-1.96267	0.0698711
Slope	0.0292019	5.7964E-3	5.03794	1.8131GE-4

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio
Model	198.34474	1	198.34474	25.38085
Error	109.40634	14	7.81474	
Total (Corr.)	307.75108	15		

Correlation Coefficient = 0.802806
Stnd. Error of Est. = 2.79549

Regression analysis on 115 $^{\circ}$C temperature and 4% moisture condition of bond formation