

**CURE OF AQUEOUS PHENOL-FORMALDEHYDE RESIN AT ELEVATED
WATER VAPOR PRESSURES**

by

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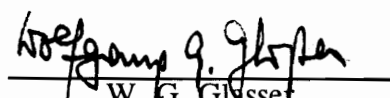
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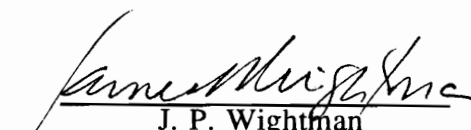
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(ABSTRACT)

The intent of this research was to enhance our knowledge of aqueous phenol-formaldehyde resin cure as it is affected by the elevated water vapor pressures that occur during hot-pressing of a wood-based composite. Microdielectric spectroscopy (DEA) was used to monitor the cure reaction, and thermomechanical analysis (TMA), swelling tests and scanning electron microscopy (SEM) techniques were used to characterize the final resin-network. Microdielectric results showed that as the water vapor pressure of the system increases the time to gelation increases. It was also found that the injection of saturated water vapor sharply decreased the gelation time when compared to the other water vapor environmental conditions. In addition, it was found that the higher the water vapor pressure the lower the residual ion viscosity. Thermomechanical analysis and swelling test experiments showed that as the water vapor pressure increases the glass transition temperature and the cross-link density of the cured resin-network decreases. Considerable differences in the morphology of the network were found using SEM. Thus, it can be established that during the curing process under elevated water vapor pressures of a liquid phenol-formaldehyde adhesive some water is trapped into the resin network and it is acting as a plasticizer.

A theoretical approach to model the cure kinetics of phenol-formaldehyde has been developed. The model is based on the occurrence of two simultaneous processes (condensation polymerization and evaporation of water) and on the concentration dependency of the activation energy of polymerization.

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CHAPTER 1

Introduction

Over 75% of all wood used in the United States involves some form of adhesion. Adhesives for wood products and construction make up 25% of the total adhesive manufactured in the United States (79). Phenol formaldehyde (PF) adhesives are extremely important in the wood composite industry, because of their resistance to high moisture environments (69, 70). The polymerization of aqueous phenol-formaldehyde is a condensation reaction. The water must be substantially removed from the liquid phase to accelerate the reaction (71). Furthermore, water may play a role in the resulting chemical structure (i.e., crosslink density) due to effects on molecular mobility during polymerization (27). This reaction presents problems in terms of characterization as a result of the phase transformation from liquid prepolymer to an insoluble network. The phase transformation makes inviable the use of many conventional analytical techniques to study the polymerization reaction occurring beyond gelation (21). On the other hand, there are several factors, other than temperature, affecting the curing rate of phenol-formaldehyde adhesives; molecular weight distribution, resin concentration, formaldehyde to phenol molar ratios, and additives (highly reactive compounds and catalyst) (66). All these complexities make the kinetics of curing still largely unexplained. Knowledge of phenolic chemistry, structure, characteristic reactions, and kinetic behavior remains an invaluable asset to the adhesive formulator in designing resins with specific physical properties. Modelling the process of cure is of great interest from a practical point of

Introduction

view because the process can be simulated. Thus, the best operational conditions can be determined.

To the present, research on characteristics of adhesive curing has been done mainly under atmospheric pressure at moderate or low humidity. Thus, the achievements are not applicable to the prediction of curing conditions during hot-pressing of wood composites. It is therefore important to define the cure kinetics of thermoset adhesives considering pressures above 1 atm in high moisture environments.

Thus, the overall project goal of this research is to enhance our knowledge of aqueous phenol-formaldehyde resin cure as it is affected by elevated water vapor pressures that occur during hot-pressing of a wood-based composite. The specific objectives of this research are:

1. To characterize the polymerization reaction of aqueous phenol-formaldehyde thermosetting adhesive above atmospheric pressure using microdielectric spectroscopy and gelation time measurements.
2. To determine if water vapor pressure influences the chemical structure and morphology of cured phenol-formaldehyde resin.
3. To develop a theoretical model of the cure kinetics of aqueous phenol-formaldehyde thermosetting adhesives in a pressurized water vapor environment.

CHAPTER 2

LITERATURE REVIEW

Phenol-Formaldehyde Reaction Mechanism

A phenol-formaldehyde (PF) resin is a mixture of polymer molecules differing in molecular weights, shapes, and degree of substitution with methylol groups and methylene linkages. Phenolic resins are obtained by step-growth polymerization of difunctional monomers (aldehydes) with monomers of functionality greater than 2 (phenol) (1,2). A large number of resins with different properties are possible, depending upon the type of phenol used, the formaldehyde-to-phenol ratio, the type and amount of catalyst and/or hardener used, and the total reaction time (3,4). PF resole resins are obtained as a result of alkaline catalysis and an excess of formaldehyde.

P/F molar ratios between 1:1.0 to 1:3.0 are customary. These resins are mono - or polynuclear hydroxymethylphenols (HMPS) which are stable at room temperature, but are transformed into three dimensional, crosslinked, insoluble, and infusible polymers by the application of heat (1). This transformation takes place in three stages: 1) A stage-liquid or solid material which is generally soluble and fusible; 2) B stage-liquid or solid material, insoluble but swelled by solvent, and softened by heat; 3) C stage-insoluble and infusible (4,5).

In the first stage of the reaction, formaldehyde merely adds itself onto the phenol molecule without losing any atoms. The initial attack may be at the 2-, 4-, or 6-position. In the second stage of the reaction, the formaldehyde splits off its -OH group (hydroxyl

group), which then takes a -H atom from a passing phenol molecule and forms a water molecule. Meanwhile the points or sites on the two phenol molecules which originally held the -OH and the -H are extremely reactive and strongly attracted to each other. They form a bond as soon as they can get close enough together and in the proper orientation with respect to each other. The resulting connection produces what is called a "methylene bridge" between two phenol molecules (Figure 2.1a). This type of connection, being covalent and carbon to carbon, is considered to be the strongest and most durable that can be formed between two organic molecules (6).

It is important to mention that in the second step, it is also possible to form methylene ether linkages (Figure 2.1b). At temperatures above 150°C methylene ether linkages can lose formaldehyde and convert to methylene linkages (3,7). Pizzi (3) pointed out that ether can be formed only within limited and critical pH ranges, and then only at slow rates. Thus, the formation of many ether links is unlikely.

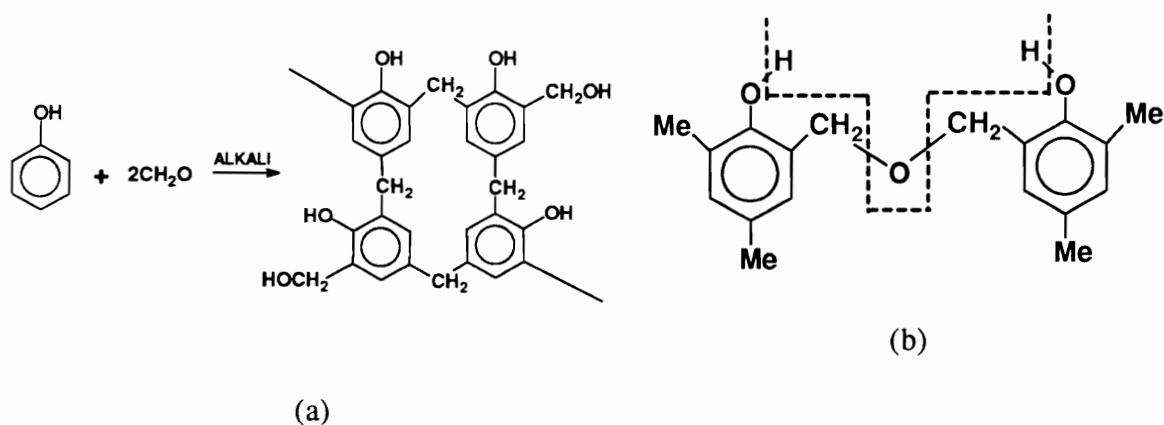


Figure 2.1. Reaction of phenol with formaldehyde (a) and methylene ether linkage (b).

Lilley and Osmond (8) separate the mechanisms of condensation of phenol with formaldehyde into two phases. In the early stages, when water is present, condensation is almost definitely ionic. At a later stage after dewatering, the reaction proceeds in unreacted phenol as the solvent (or in the final stage when reaction is mainly in molten polymer), where the reaction is almost definitely nonionic. These authors formulate the reaction mechanisms as shown in Figure 2.2.

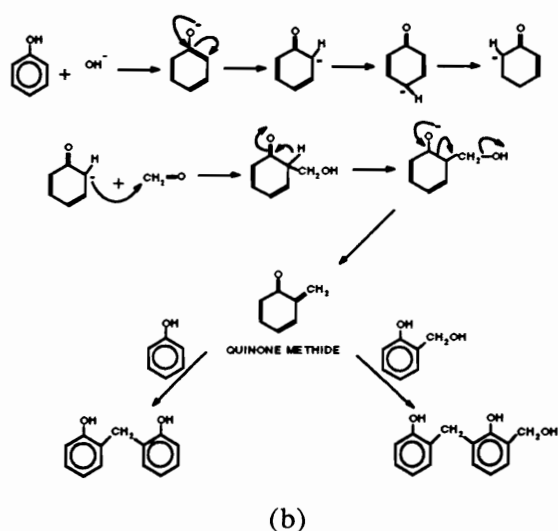


Figure 2.2. The reaction mechanism (quinone methide intermediate).

Referring to the nonionic mechanism, Lilley (8) shows that since the reaction cannot involve a carbonium ion, it will probably use an intermediate of the quinone methide type. This compound is probably generated by a hydrogen-bonding mechanism.

Theory of Thermoset Resins

When sufficiently frequent branching or crosslinking of chains occurs during the course of a polymerization or polycondensation reaction, the enhanced capacity for further growth of the larger molecules (due to their larger number of unreacted end groups) leads ultimately to the formation of a few network structures so huge that the material changes rather abruptly from a fluid to a gel (94). Flory (95) developed a statistical approach for predicting the extent of reaction at which gelation occurs. At any point in the polymerization reaction, a polyfunctional system may be characterized by a branching coefficient, α . This parameter depends on the extent of the reaction, F . The branching coefficient is defined as the probability that a given functional group of a branch unit leads via a chain of bifunctional units to another branch unit. If this probability is larger than the probability that the chain will terminate as a loose end, the system is a gel (80).

In Flory's work, the observed gel point was always found to be higher than the gel point calculated by his theory of infinite network formation. Bobalek et al. (81) conducted an investigation with a model resin system and appear to have resolved this discrepancy. Using glycerol, phthalic anhydride and lauric acid as their reactive system, they found that the formation of macroscopic network molecules occurred near the gel point predicted by Flory. Because of their large size, these molecules tended to precipitate out as microgel particles which remained suspended in the lower molecular-weight polymer fractions. As the observed gel point is approached, the concentration of these microgel particles increases until they come into contact and interact. At the classically-observed gel point, the microgel flocculates and becomes a continuous phase,

causing the expected steep rise in viscosity (81).

The other critical event which takes place during the cure of thermosets is vitrification, which occurs when the material undergoes a transition from a soft elastomer to a rigid glass. The rate of the curing reaction is drastically decreased when the resin reaches the vitrification stage. At this point, the resin has undergone enough crosslinking to completely immobilize the reactive chains within the network (9).

Unlike gelation, vitrification is a reversible process. The crosslinking resin can usually be devitrified by raising the temperature above the T_g of the partially cured resin. The material once again becomes elastomeric and is capable of exhibiting a relatively rapid reaction rate. The material may react at this temperature until the crosslinking polymer chains once again reach a new vitrification stage. Thermoset resins may exhibit this shifting glass transition behavior until an upper limit is reached (13). Gillham characterized this temperature as $T_{g\infty}$, or the glass transition of the fully-crosslinked system. If the material is exposed to temperatures greater than $T_{g\infty}$ for significant periods of time, the material is susceptible to decomposition reactions (28).

Time-Temperature-Transformation Cure Diagram

The time-temperature-transformation (TTT) cure diagram provides a convenient means of visualizing the transformations that take place during the cure of a thermosetting resin. Gillham used torsional braid analysis and other methods to measure the times to gelation and vitrification at various isothermal cure temperatures (82,83). Figure 2.3, termed a TTT diagram by Gillham, illustrates the major features of such data.

The TTT diagram shows that the time to gelation increases as the cure temperature is lowered. This is expected for a thermally activated rate process. The S-shape vitrification curve reflects the competition between the usual tendency of rising temperature to soften the material and the role of increasing reaction rate to accelerate the curing reaction and harden the material by cross linking. The temperature at which even the completely uncured resin vitrifies is T_{g0} , and $T_{g\infty}$ is the temperature of the fully cured resin. The value of $T_{g\infty}$ is of considerable practical importance, as it is the softening temperature of the fully cured adhesive, and thus limits its useful temperature range for most applications. The vitrification curve must remain between these limiting temperatures.

The diagram is also valuable as a processing aid. The temperature at which the gelation and vitrification lines cross (gel- T_g) indicates the upper temperature at which the resin can be stored. Once the resin has gelled the material cannot be further processed. At temperatures less than the gel- T_g , vitrification occurs before gelation. Because vitrification quenches the cross-linking reaction, gelation is avoided and the material remains processible.

Thermal degradation can also take place during cure, due to a variety of chemical mechanisms that include oxidation or chain scission. This degradation takes place at a rate that decreases exponentially with temperature, just as the cross-linking reaction does. Accordingly, the time to excessive degradation can be plotted on the TTT diagram along with gelation and vitrification curves, and this line is denoted "char" in Figure 2.3.

Hofmann (63), Niranjan (85) and Toffey (86) have constructed TTT diagrams for

different systems using dynamic mechanical thermal analysis (DMTA).

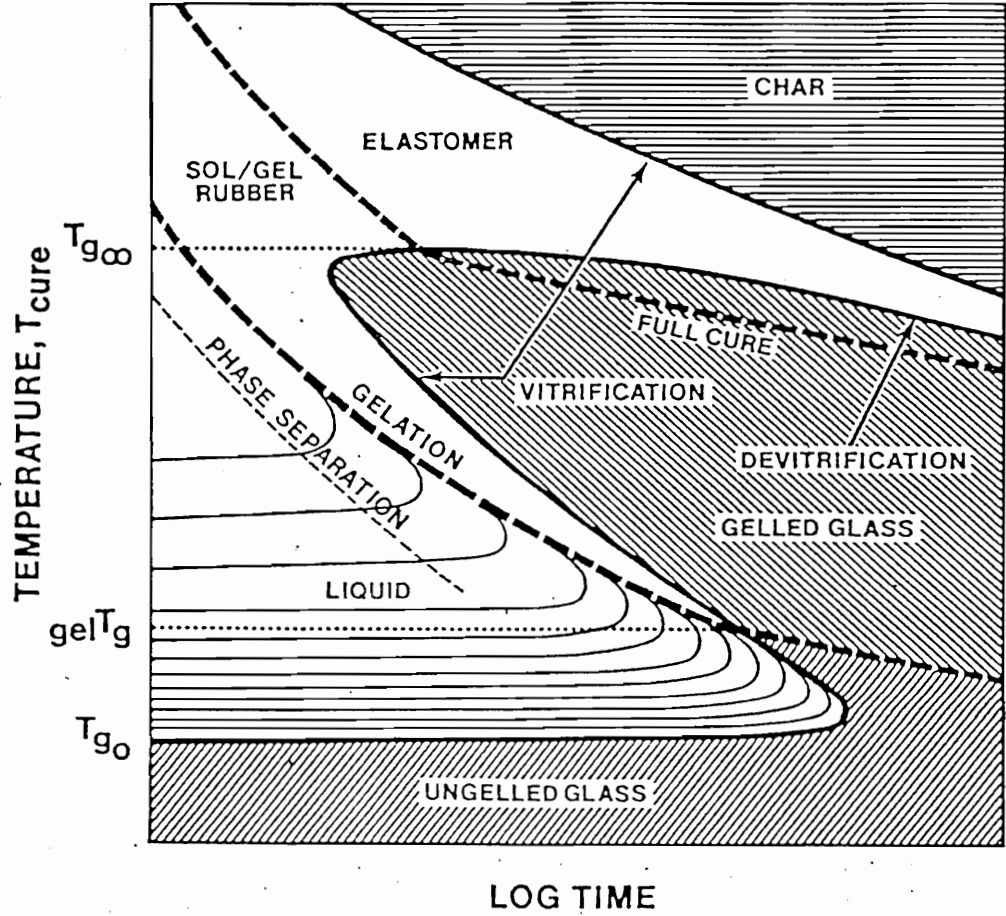


Figure 2.3. Time-temperature-transformation diagram for isothermal cure.

Swelling of Cross-Linked Polymer Networks

In the field of high polymers there are numerous examples of materials which absorb large quantities of suitable solvents without dissolving. Vulcanized rubber, vinyl-divinyl copolymers, and lightly gelled thermosetting resins when placed in solvents swell through imbibition to a degree depending on the solvent and the structure of the polymer. The original shape is preserved, and the swollen gel exhibits plastic rather than elastic properties (87).

This phenomenon of limited swelling is characteristic of polymers possessing network structures. If the network structure is permanent in the sense that its essential skeletal structure is not disrupted by the action of the solvent, a state of equilibrium swelling may be attained. As more and more solvent is absorbed by the polymer the network is progressively expanded. The chains connecting multifunctional network junction points are forced to assume more elongated, less probable, configurations. Consequently, a decrease in chain configurational entropy is produced by swelling. Opposing this, an increase in entropy of mixing of solvent with polymer accompanies swelling. Equilibrium will be attained when these opposing entropies become equal in magnitude.

The interaction of polymers with low molecular mass solvents, resulting in limited or unlimited swelling, has long been the subject of investigation from theoretical and practical points of view (87-90). There have been notable efforts to find a relation between the equilibrium swelling behavior and structural parameters, such as extent of crosslinking of a homogeneous polymer network (89) or of a heterogeneous network (90).

The equilibrium swelling behavior of a polymer has been also used to determine the solubility parameter, interaction parameter, molecular conformation, and thermodynamic flexibility (91,92). Further, there are many papers where swelling data were fitted to various swelling models for testing the reliability of the proposed swelling model (90,91,93) or dissolution model (94).

Determination of the Kinetics of Cure

The cure process can be visualized on a molecular level as converting small molecules to large molecules through the processes of chain extension, chain branching, and crosslinking with the buildup of a three-dimensional network of infinite molecular weight (9). A number of techniques have been developed to measure the cure of phenolic resins as they progress through the A, B, and C stages. These techniques usually relate to a number of combined physical and chemical properties of the phenolic including molecular weight, molecular weight distribution, viscosity, chemical structure, and rate of cure (8).

Newer analytical methods have been developed throughout the 1970's. Among these methods are nuclear magnetic resonance (NMR), gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). However, most of these methods are only useful for measuring the changes which occur during the early stages of chain-extension and cross-linking reactions. As such, they need not relate directly to the ultimate performance characteristic of a fully cured system. A number of new techniques are now available that offer opportunities for the understanding of the chemistry during

the later stages of chemical reaction of phenolic resins. These include solid-state nuclear magnetic resonance and dynamic mechanical analysis (DMA).

Thermomechanical Analysis (TMA)

TMA is used to measure the change in dimension of the sample material as a function of temperature and stress. Using this technique, the degree of crosslinking in a resin can be established through detecting the glass transition, T_g . Moreover, the coefficient of expansion of the pre-impregnated material can be measured before and after T_g . TMA is also able to study how material samples behave under strain. Thus, the thermomechanical system can measure the static properties of a material, and its changes with temperature (10).

Mizumachi and Saito (43) using thermal analysis found that this technique is a useful tool to trace directly the chemical reaction with time, because a signal in the equipment is directly proportional to the thermal change due to the chemical reaction in the sample cell. Also, Mizumachi and Morita (44) studied the curing reactions of a commercial phenolic resin mixed with various wood powders using differential thermal analysis. They determined the activation energies of the reactions. A curing study of phenol-resorcinol-formaldehyde resins using thermal analysis was developed by Chow (45). The reaction was shown to take place in two stages. The first stage involved an exothermic reaction and the second stage involved an endothermic-dehydration reaction.

Differential Scanning Calorimetry (DSC)

The DSC technique has been used by many authors to study PF systems. Erä (23) used DSC (sealed sample cells) following the cure of resol. The study examined several PF resols with PF ratios of 1: 1.5 to 1:2.1. He found that the heat of reaction correlated with PF mol ratio with lower value for higher PF ratio. Zaks et al. (24) studied the thermal degradation of the char-forming phenol-formaldehyde resins to provide information for the systematic design of high temperature flame-resistant phenolics. A technique to determine the chemical cure of resins was developed using differential scanning calorimetry (DSC) by Geimer et al. (25). The same authors (27) used different techniques to characterize the structure and chemistry of phenol-formaldehyde resol resins during synthesis, aging, and cure. The degree of cure was measured using DSC. Finally, DSC has been used successfully to compare the performance of different polymer compounds (epoxy systems, and Polyamide systems) (28). Also, Geimer and Christiansen (26) developed new techniques to relate the curing and bonding characteristics of a resin to time-dependent changes in temperature and moisture. The chemical cure pathway was determined using DSC.

Dynamic Mechanical Testing

Dynamic mechanical analysis (DMA) and torsional braid analysis (TBA) provide a measure of the mechanical response of a material as it is deformed under periodic stress. These techniques detect all motional transitions and usually provide the most sensitive means of studying glass and secondary transitions, and of quantitatively determining the

effects of phase type and morphology of properties (10, 11, 13, 14). The DMA method has been used to measure the cure time, vitrification time, and other useful cure parameters of phenol-formaldehyde resins as affected by the temperature and resin composition. The method has been useful in optimizing the synthesis and curing parameters of PF resin adhesives (49, 50).

Young et al. (4) evaluated and compared a series of selected commercial phenolic resins used for paper impregnation using isothermal DMA. They were able to obtain relative cure velocities, melting range, modulus vs. temperature information, cure gel point and information on cross-linking chemistry.

Myers et al. (27) measured the degree of cure developed during constant heating rate DMA scans of two different phenol-formaldehyde resole resins for a series of maximum DMA temperatures. They found that water loss greatly complicated interpretation of DMA temperature scans. In addition, Geimer and Christiansen (26) related the cure response of phenolic resins to bond strength development in controlled isothermal and isohydro conditions using DMA. Hofmann (63), using the same technique, monitored the cure of an epoxy-amine system. Modulus-temperature characteristics and phase separation for thermoplastic adhesives have been studied using DMA by many authors (51, 52, 53).

Rigidity and damping changes for phenol-formaldehyde, urea-melamine-formaldehyde, crosslinking polyvinylacetate and phenol-resorcinol-formaldehyde, during and after cure have been determined using TBA (14). Gillham (40) studying the isothermal cure of epoxy systems found that both gelation and vitrification can be

detected during the thermosetting process using TBA. Also, Warfield and Lee (41) in a TBA study of cured phenolic resin found that three secondary transitions occurred over the temperature range of 123 to 623 K the largest of which occurs at about 393 K. These transitions were discussed in terms of polymer structure. TBA is employed in the characterization of thermoplastic and thermoset coatings consisting of single or multiphase systems. On the other hand, Enns and Gillham (42) have developed a time-temperature-transformation cure diagram which fully described gelation and vitrification of an epoxy system based on TBA measurements.

Nuclear Magnetic Resonance (NMR)

NMR deals primarily with liquid or solution systems. Although, NMR studies of solids are of increasing importance since the development of special techniques which allow high resolution to be attained (11, 12, 35). Kim et al. (34) studied the NMR spectrum of various phenol-formaldehyde resins containing different amounts of water and caustic. Also, through the use of NMR, relative comparisons were made for the degree of polymerization of acetylated phenol-formaldehyde resins prepared with different molar ratios by Steiner (36). Sojka, et al. (57) used NMR spectroscopy to study the reaction of phenol and hexamethylenetetramine. The crude time dependence of NMR signals enabled a qualitative evaluation of rate processes occurring in the reaction. In addition, Kopf and Wagner (37) successfully utilized NMR to study the reaction of phenols with curing agents and were thus able to identify reaction intermediates such as oxazines and benzylamines. Moreover, Myers et al. (27) studying NMR spectra of two different

phenol-formaldehyde resol resins found that these resins differed significantly in relative amounts of hydroxymethyl groups and methylene linkages. The condensation reaction between phenol, melamine and formaldehyde in relation to pH was analyzed by means of NMR by Braun and Kraube (38).

Improvement in NMR instrumentation has allowed the analysis of resol cure with particular reference to extensive involvement of the phenolic hydroxyl group, and the condensation/crosslinking of the methylene bridge with formaldehyde or with the hydroxymethyl group (39, 48).

Fourier Transform Infrared Spectroscopy (FTIR)

All IR spectroscopic techniques obtain a plot of some function of radiation intensity versus frequency. The manner in which this is accomplished in FT-IR is quite different from what is done in dispersive IR. In the dispersive system, radiation from the IR source is dispersed by wavelength using prisms, and slits are used to select an increment of the energy by wavelength and to define the spectral element (15,16,17).

An FT-IR basically consists of two parts: 1) an optical system which uses an interferometer and 2) a dedicated computer. The computer controls optical components, collects and stores data, performs computations on data, and display spectra.

For FT-IR, the beginning and end of the optical path are virtually identical to those of dispersive IR, that is, IR source and detector. The other optical components are quite different.

The real advantages of a FT-IR system is the Michelson interferometer that

replaces the dispersive element and slits of the conventional dispersive IR spectrophotometer. Light from the source passes through the beam splitter that reflects a portion of the beam toward a movable mirror and transmits the remainder to a fixed mirror. Upon returning to the beam splitter, the two components interfere constructively or destructively depending on the optical path difference (retardation) and the wavelength of the light (15,16,18,19).

The application of FT-IR to chemical systems has had a remarkable growth in the last 20 years. The applications include studies made on transient systems, pollution of gases, liquid chromatography, surface studies and planetary atmospheres (54,55,56).

Sojka et al. (57) studying the reaction of phenol and hexamethylenetetramine using FTIR found that bands attributable to hexamethylenetetramine and those of phenol were decreasing with time. However, bands attributable to reaction intermediates or products were not discernible. They pointed out that this problem could be due to interference from the infrared bands of starting materials. Enns and Gillham (42) measured successfully the times to gelation and to vitrification for the isothermal cure of an amine-cured epoxy using FT-IR. They did not report any problem due to interference. The application of FT-IR to the study of mechanical degradation of polymers and the post cure of composite materials was made by Fanconi (15). This author pointed out that the improved signal-to-noise of FT-IR together with digital data manipulations provide a powerful technique for characterizing the chemical and physical structure of polymeric materials. On the other hand, Myers et al. (27) conducted a preliminary evaluation of the utility of FT-IR in measuring the relative degree of cure achieved by phenol-formaldehyde

resins as hot-pressing variables changed. They reported difficulties in attempting to quantify the spectra to define changes during cure.

Microdielectric Spectroscopy

Dielectric spectroscopy is based on the interaction of electromagnetic radiation with the electric dipole moments of the material under test. The frequency range of the radiation is between 10^6 Hz and about 10^{10} Hz. Above 10^{10} Hz, in the infrared optical and ultraviolet region, the absorption and emission of radiation is due to changes in the induced dipole moments, which are dependent on the polarizability of the atoms or molecules. At lower frequencies, the contribution of the induced dipole moments becomes small in comparison with that of the permanent dipole moments of the system. Consequently, dielectric spectroscopy is useful for studying polar molecules in the gaseous phase or in solution, where absorption of radiation is mainly due to the reorientation of permanent dipoles (20). Although dielectric analysis is an old technique, recent advances in microsensor technology have allowed it to be used with remote probes and automated data acquisition systems. The ability to detect characteristics representative of molecular mobility beyond the vitrification stage, in conjunction with in situ capability, presents a promising technique for PF resin characterization that has not been available in the past.

The dielectric parameters, permittivity and dielectric loss factor, measured by this technique can be related to more common measures, such as viscosity, making it suited for both fundamental and applied investigations of the chemorheology of the curing

reaction (21). Thus, the basis of microdielectric spectroscopy is the measurement of dipole orientation and ion mobility. The permittivity, ϵ' , is a measure of the degree of alignment of dipoles, and the dielectric loss, ϵ'' , is a measure of the energy expended to align dipoles and move ions (22). Above the glass transition, ϵ'' is used to calculate the bulk ionic conductivity, using the equation

$$\sigma = \epsilon'' \omega \epsilon_0 \quad (2.1)$$

where σ is the ionic conductivity, ω is the angular frequency ($2\pi f$), f is the frequency and ϵ_0 is the absolute permittivity of free space (8.85×10^{-12} F/m) (68). Bulk ionic conductivity can be used to follow the rheological changes that takes place during the processing of thermoplastics and the curing of thermosets. Because of its relationship to viscosity, the absolute value of the ionic conductivity is termed the ion viscosity. This transformation provides a direct, rather than inverse, relationship with conventional rheological measurements.

The dielectric spectra of some anhydride cured epoxy resins have been studied by Blyachman et al. (1970). The effect of the molecular weight of the epoxy resins on the dielectric spectrum was reported by Antonov et al. (1966). Haran et al. (1965) measured the change of the dielectric loss tangent of epoxy resins as a function of the cure time at fixed frequency and temperature. The same studies were carried out using phenol-formaldehyde resins by Van Beek (58).

Recently, Kranbuehl et al. (59) successfully used dielectric analysis to study the chemistry and rheology of thermosets during cure. Also, Rials (21) studied the influence

of prepolymer functionality and pH conditions on the curing behavior of phenol-formaldehyde resins using microdielectric spectroscopy. He pointed out the utility of this method to the study of phenol-formaldehyde resin cure rheology. The same author (22) using this technique with tannin-modified phenol-resorcinol-formaldehyde resins pointed out the capability to monitor resin cure in the bond line. Connolly and Tobias (60) obtained thermal scans for a thermoset prepreg resin using dielectric thermal analysis (DETA). The authors pointed out that DETA is able to reveal material properties over 1 nm.

Viscosity and Gelation Time Measurements

In this technique viscosity changes accompanying a physical or chemical event in the sample are monitored either as a function of temperature or time. Viscosity is measured with either a conventional viscometer or a cone and plate viscometer. This simple technique indicates the original state of the material (resin) and provides information concerning reactivity during the initial stages of cure.

Tohmura et al. (64) studied the overall kinetics of the curing of phenol-formaldehyde resin adhesives and the relationships between the curing rates and resin formulation variables measuring changes in viscosity. They found that the overall reaction of gel formation was of second-order with respect to the resin concentration.

The influence of environmental (oil-bath) temperature and adhesive temperature on gelation time of different types of adhesives was studied by Subiyanto et al. (65). They found that the gelation rate and average temperature of adhesive didn't show a

significant relationship. Higushi et al. (66) investigated the effect of the degree of condensation of phenolic resins in the A stage on the rate of cure using viscosity and gelation time measurements. In addition, Ballerini and Valdes (67) studying the effect of environmental temperature on gelation time of urea-formaldehyde found that the relationship between gelation rate of the adhesive and environmental temperature obey an Arrhenius equation.

It has been discussed that in order to obtain a comprehensive view of the cure process, it is necessary to characterize both the physics and chemistry of crosslinking systems. The most important characterization methods that respond to the chemistry and physics of the cure process have been described. These methods can be summarized as follows:

- Chemical

- Differential Scanning Calorimetry (DSC)

- Fourier Transform Infrared (FT-IR) Spectroscopy

- Nuclear Magnetic Resonance (NMR) Spectroscopy

- Physical

- Dynamic Mechanical Testing (DMT)

- Microdielectric Spectroscopy (DETA)

- Thermomechanical Analysis (TMA)

- Viscosity and Gelation Time Measurements

Modelling The Cure Kinetics

There are several factors which are considered to control or affect the curing-rate of alkaline phenol-formaldehyde resin adhesives. These are the molecular weight of the resin, molecular structure, composition of chemical species, catalysts, additives, temperature and rate and extent of solvent loss.

Modelling the process of cure is of great interest both from a theoretical point of view or for practical and industrial applications. The process can be simulated and comparisons made between the experimental and calculated results to test, not only the validity of the model, but also the accuracy of the thermal and kinetic parameters. Simulating the process is necessary to determine the best operational conditions when the process of cure must be developed on a larger scale. However, an important problem must be considered, namely the selection of a kinetic equation of the overall cure reaction and the determination of the kinetic parameters. The cure kinetics can be described using a general n th order rate equation (9),

$$\frac{dF(t,T)}{dt} = k(T) [1 - F(t,T)]^n \quad (2.2)$$

where $F(t,T)$ is the fractional extent of conversion, n is the order of the reaction, $k(T)$ is the rate constant, t is the time, and T is the absolute temperature. The Arrhenius equation gives the temperature dependence of the rate constant,

$$k = A \exp(-E/RT) \quad (2.3)$$

where A is the Arrhenius frequency factor, E is the activation energy, and R is the gas

constant. Combining Equation (2.2) and (2.3):

$$\frac{dF(t,T)}{dt} = A \exp \left(- \frac{E}{RT} \right) [1 - F(t,T)]^n \quad (2.4)$$

Integration of Equation (2.4) provides a generalized non-isothermal expression for the fractional conversion in terms of the kinetics parameters n , E and A :

$$F(t,T) = 1 - \left[(n - 1) A \int_0^t \exp \left[- \frac{E}{RT(t)} \right] dt + 1 \right]^{1/(1-n)} \quad (2.5)$$

Taking the logarithm of Equation (2.4),

$$\ln \left[\frac{dF(t,T)}{dt} \right] = \ln A - \frac{E}{RT} + n \ln [1 - F(t,T)], \quad (2.6)$$

provides a form suitable for multiple regression analysis:

$$z = a + bx + cy \quad (2.7)$$

where $a = \ln A$, $b = -E/R$, and $C = n$. The reaction kinetics parameters n , E and $\ln A$ are obtained simultaneously from this expression using a linear multiple regression analysis. The fractional extent or degree of cure is obtained from one of the techniques previously described.

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CHAPTER 3

CHARACTERIZING THE CURE REACTION OF AQUEOUS PHENOL-FORMALDEHYDE USING MICRODIELECTRIC SPECTROSCOPY.

Introduction

During hot-pressing of a wood-based composite, the gas pressure in the mat is primarily the result of evaporating moisture. Amount and distribution of moisture in the mat significantly affect the rate and degree of adhesive cure. For the polymerization of aqueous phenol-formaldehyde to occur water must be substantially removed from the liquid phase (1). Characterization of this reaction is difficult because the reaction mechanism is complex and sensitive to the surrounding environment (wood chemistry, temperature, vapor pressure, etc.). Analytical techniques are available to characterize these systems, but few efforts have been made to monitor the cure kinetics in elevated water vapor pressure environments.

Microdielectric spectroscopy is a technique that provides information on material viscosity prior to vitrification and material rigidity in the glassy state. Microdielectric sensors are now available which function down to frequencies characteristic of mechanical measurements (less than 1 Hz) and can be inserted directly into curing composites structures. By monitoring the dielectric properties (permittivity and loss factor) at several frequencies, the ionic conductivity can be extracted with the aid of commercial software packages in real time (2). This technique has been used successfully to study the chemistry and rheology of thermosets during cure at atmospheric conditions (3-5).

Nevertheless, the achievements are not fully applicable to the understanding of curing conditions during hot-pressing of wood composites. The intent of this paper is to enhance our knowledge of aqueous phenol-formaldehyde resin cure as it is affected by the elevated water vapor pressures that occur during hot-pressing.

Principles of Microdielectric Spectroscopy

When an insulating material is subjected to an applied electric field, charge separation and molecular rearrangements occur within the material, causing the phenomenon of polarization. The magnitude of the polarization is measured as a property of the material called the dielectric constant. This macroscopic property is related to the molecular structure of the dielectric through the molecular polarizability and the molecular dipole moment (6). Since the magnitude of the dielectric constant is related to the molecular structure, its dependence on time, frequency, and/or temperature generally reflects molecular motion. Dielectric analysis may therefore be used to probe the chemistry, rheology, and molecular mobility of polymeric materials. This technique measures the fundamental characteristics of a material; capacitance, or its ability to store electric charge, and conductance, or its ability to transfer electric charge, as a function of time, temperature, and frequency. Four major properties are reported in dielectric analysis: permittivity (ϵ'), loss factor (ϵ''), dissipation factor (ϵ''/ϵ'), and ionic conductivity (σ). ϵ' is proportional to capacitance, and ϵ'' is proportional to conductance. Ionic conductivity is derived from measurement of ϵ'' . Dielectric cure monitoring of a thermoset relies on measuring changes in ϵ'' , which is itself conveniently divided into two

parts as shown below:

$$\epsilon'' = \frac{\sigma}{\epsilon_0 \omega} + \frac{(\epsilon_r - \epsilon_\infty)(\omega \tau)}{1 + (\omega \tau)^2} \quad (3.1)$$

where ϵ_∞ is the high frequency permittivity (unrelaxed permittivity), ϵ_r is the low frequency permittivity (relaxed permittivity), ω is the applied field frequency, τ is the dipole relaxation time, and ϵ_0 is the permittivity of free space. The first term on the right side of equation 3.1 refers to the portion of dielectric loss which arises from ionic conduction. The second term on the right describes the energy lost or work expended during the orientation of permanent dipoles exposed to an oscillating electric field of frequency $\omega/2\pi$.

At low frequencies the ionic contribution is much larger than the dipole contribution and the ionic conductivity, σ , can be obtained (See Equation 2.1). It has been shown that the ionic component of the loss is a sensitive measure of thermoset cure and that ionic conductivity is a direct measure of molecular viscosity (7). At the beginning of the polymerization reaction, the viscosity of the prepolymer mixture is low, so that the dipoles reorient quickly and τ is short. As the polymerization proceeds or as the molecular weight increases, the viscosity increases. Dipoles, which are present in the prepolymers, exhibit a transition from an unhindered to a hindered state as molecular weight increases. Ions, which are usually present as impurities, initially exhibit high mobility (as measured by electrical conductivity), but become slow as polymerization proceeds. During the polymerization reaction in the presence of an alternating electric field, the dipoles and ions move more slowly relative to the frequency of the applied field and, eventually,

reach a random condition as the polymer network forms.

Materials and Methods

Material

A commercial liquid phenol-formaldehyde resol resin, with a 45% non-volatiles content, a viscosity of 300 cps at 25 °C, a number-average molecular weight of $1.6 \cdot 10^3$, a weight-average molecular weight of $1.9 \cdot 10^4$, and a pH value of 11.2 at 25 °C was used. The resin was supplied by Georgia-Pacific Resins, Inc., and is representative of a typical core resin used in the manufacture of oriented strand board.

Microdielectric Analysis

To monitor the polymerization reaction, a curing vessel was housed inside a 600 ml Parr reaction vessel. This small reactor was connected to a larger vessel, which served as a source of controlled steam pressure. A vacuum pump was used to reach -97 kPa vacuum conditions in the small reactor. Then, saturated water vapor was injected till a complete water vapor environment at 97 kPa was obtained. Heat was supplied using an electric heater. After reaching a desired environmental temperature, the resin (8 ml) was injected by a syringe through a port in the reaction vessel and into the 60 ml glass curing vessel contained in the reaction vessel. The reaction vessel was then rapidly pressurized with saturated steam to the desired pressure. A computer-based data acquisition system simultaneously monitored the resin temperature, the environmental temperature, and the internal pressure. Shielded, ungrounded, Type-K thermocouples and a pressure transducer

(Omega PX302-150GV) were used to this end. Output was recorded every 4 seconds.

A Eumetric System III DEA (Micromet Instruments, Inc.) was used to monitor the dielectric response of the cure of the phenol-formaldehyde resin. A disposable high conductivity remote sensor was passed through a 5 mm diameter copper tube inserted in the lid of the 600 ml reaction vessel. The sensor cable was sealed within the tube with an epoxy resin. This allowed insertion of the sensor element directly into the curing resin without compromising the pressure seal. Output from this connection was recorded every 6 seconds. Measurements were made at 1Hz and 100 kHz frequency. The equipment setup is shown in Figure 3.1.

The cure of the resin was monitored as a function of environmental temperature and water vapor pressure. Five environmental temperatures (100, 110, 120, 130 and 140 °C) and three water vapor pressures (partial water vapor pressure in the air, p_v ; 97 kPa water vapor pressure, and saturated water vapor pressure, p_s) were used. The value of the partial water vapor pressure in the air depends on the atmospheric conditions or the environmental conditions in the laboratory. Thus, in our case, during the time in which the experiments were carried out the conditions in the laboratory varied from 33 to 55 % relative humidity and from 22 to 25 °C dry bulb temperature. This means a range in partial water vapor pressure from 0.9 to 1.8 kPa. Therefore, for convenience, this pressure condition was defined as < 7 kPa. The saturated conditions were 97, 138, 200, 269 and 352 kPa. Three replications of each treatment combination were made.

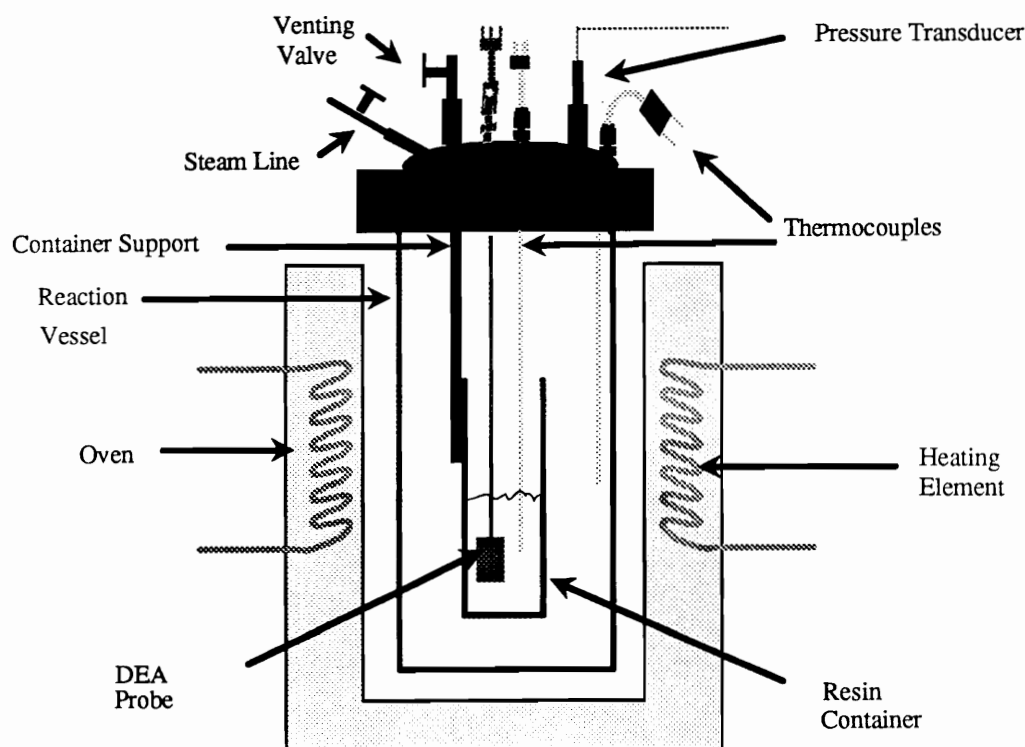


Figure 3.1 600 ml reaction vessel for dielectric experiments

Gel Time Measurements

Gel time measurements were also performed in order to have complementary information about the rate of cure of the resin system. This technique was selected because it is a simple technique that measures the viscous resistance as a result of molecular size and configuration and it can be used at an industrial level.

The methodology used for these experiments is the same as described for microdielectric analysis. The cure reaction took place in the same reactor and at the same operational conditions. In this case the adhesive was continuously stirred within the

specimen container using a shaft-driven stir mechanism that passed through the lid of the reaction vessel and into the specimen container. The gelation of the adhesive was detected by means of an encoding device attached to a constant-torque stirring mechanism, which replaced the dielectric probe shown in Figure 3.1. Temperature of the adhesive and angular rate of rotation were recorded using the same data acquisition system described previously in this paper.

As this technique was used to gather additional data about the rate of cure of the resin for comparison with the results given by the DEA technique, only one run for each condition was performed. Thus, 15 experiments were carried out.

Results and Discussion

Microdielectric Analysis

The loss factor provides large and easily discriminated signals which can be used in studying the formation of polymer networks (3, 8). As it was mentioned before, the loss factor has a dipole and an ionic contribution, and at low frequencies the ionic conductivity can be obtained. From the inverse absolute value of the ionic conductivity the ion viscosity can be derived. The ion viscosity provides a direct relationship with conventional rheological measurements thereby making the data more readily interpretable (4, 5). Thus, in these experiments the ion viscosity was chosen as the dielectric characteristic which was monitored in the cure of the aqueous phenol-formaldehyde adhesive system.

A typical DEA spectrum is shown in Figure 3.2, where the loss factor, the ion

viscosity and the adhesive temperature are plotted against time. It can be seen that the temperature of the adhesive increases till the boiling temperature of the solvent (water) is reached. The loss factor increases at the beginning of the experiment. As the temperature of the resin increases the thermal energy of the system increases, enhancing

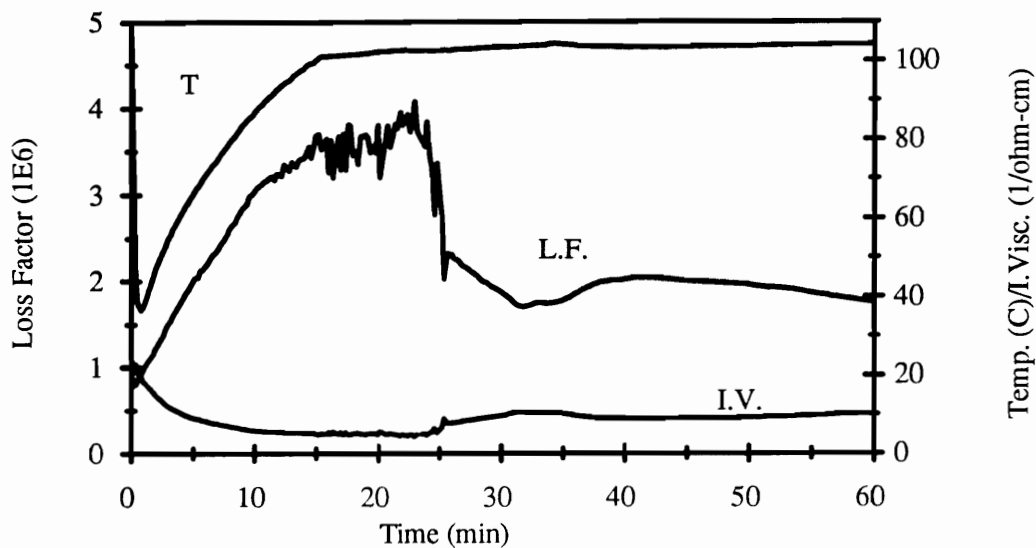


Figure 3.2 DEA spectra for a resin cured at < 7 kPa water vapor pressure and 130 °C.

the movement of ions and polymer molecules. Therefore, there is an increase of thermal losses due to friction between dipoles and transport of ions. This is corroborated by the ion viscosity signal which starts to decrease in the same way in which conventional viscosity decreases with temperature (thixotropic behavior) (9). After 15 minutes the adhesive has reached a constant temperature and both the loss factor and the ion viscosity remain constant. This behavior indicates the polymerization reaction has not yet advanced

enough to detect changes in dielectric characteristics due to cross-linking. As the polymerization reaction proceeds, generating larger molecules, the movement of the ions and dipoles in the adhesive system is restricted by intermolecular cross-linking and less thermal losses occur as a consequence of dipole or ion transport friction. Thus, the loss factor decreases and the ion viscosity increases. It is interesting to point out that the ion viscosity reached the plateau region in 10 minutes and at approximately 90 °C. This is in accordance with the results obtained by Rials (5) and the temperature value for the polymerization reaction to start given by Pizzi (10). In the graph this is an inflection point, which often indicates a turning point between two competing processes. In this case thermal thinning and polymerization.

Figures 3.3 and 3.4 show the DEA spectra for resin systems cured at 97 kPa complete water vapor environment and saturated conditions, respectively. It can be observed that changes in the environmental conditions do not change the trend of the ion viscosity signal. The DEA spectra for the complete set of environmental conditions are presented in Appendix A.

Results obtained by Kim (13) for the cure of phenolic resin at atmospheric conditions using dynamic mechanical analysis are in agreement with the results obtained in this research. They reported that the gelation time for a set of resol resins cured in the range 110 - 150 °C varied from 15 to 26 minutes.

It is known that the gel point is defined as the point at which the resin system attains an infinite value of its average molecular weight, or as the point at which the viscosity of the liquid resin begins to exhibit pseudoelastic properties (11). Thus, the gel

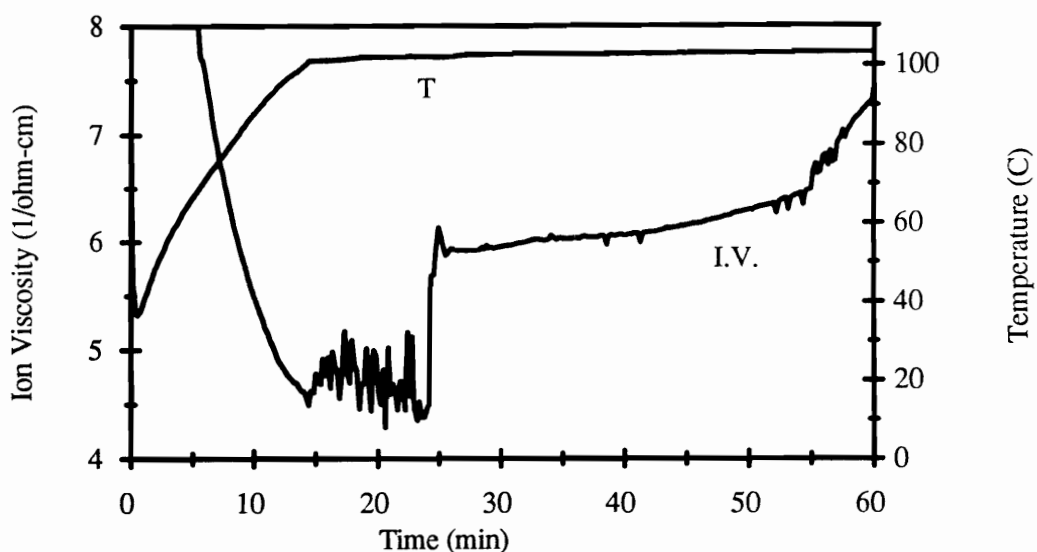


Figure 3.3 DEA spectra for a resin cured at 97 kPa complete water vapor pressure and 130 °C

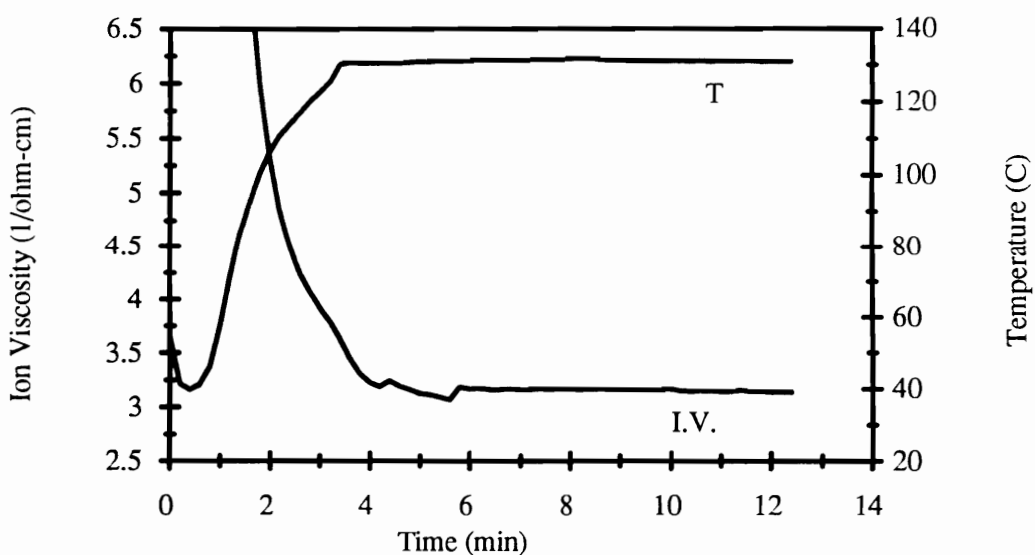


Figure 3.4 DEA spectra for a resin cured at 269 kPa saturated water vapor pressure and 130 °C

point for our system was obtained from the first inflection point of the ion viscosity signal on the plot of ion viscosity versus time (Figure 3.5). Technically, the resin has now passed from a liquid to a solid state and will no longer permit unrestricted deformations.

The resin T_g also rises as the curing reaction proceeds, because cross-linking serves to reduce molecular mobility for a given temperature. If the T_g rises enough to equal the cure temperature, the resin by definition will have vitrified (12). The reaction then becomes largely diffusion limited, with a substantial reduction in its rate. No vitrification point was detected for this system. Even though a second inflection point in some of the ion viscosity signals would indicate that vitrification was reached, the results for the glass transition temperature of the network as given by thermomechanical analysis (Chapter 4), indicate that this is not the case.

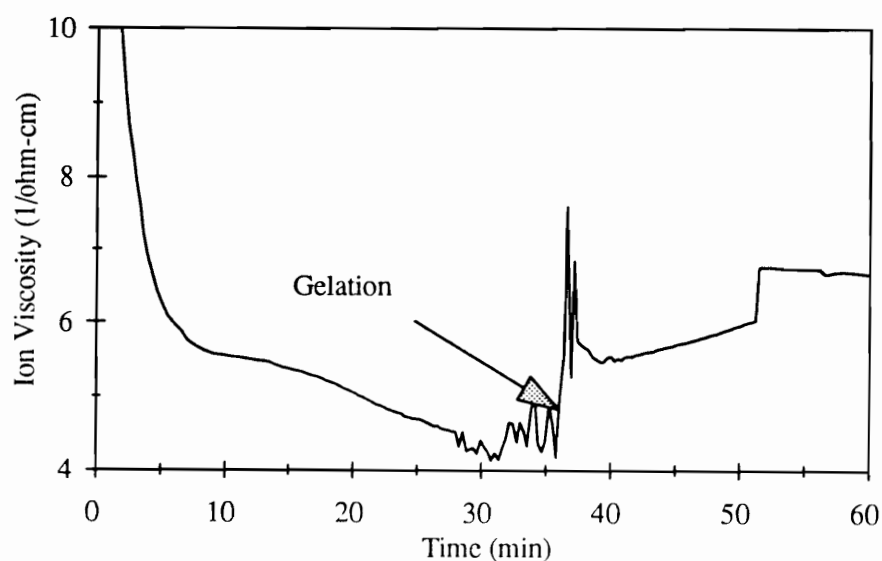


Figure 3.5 Gelation point determination (120 °C and 97 kPa)

As some problems arose in attempting to quantify gelation from some of the ion viscosity signals the information given by the loss factor signal was also considered to define this value as a way to avoid uncertainties and have reliable data.

Gelation times (t_g) obtained using this technique for different water vapor pressures are presented in Table 3.1. The temperature in this table corresponds to the temperature of the environment.

Table 3.1 Gelation time from DEA

T (°C)	$p_v < 7 \text{ kPa}$	$p_v = 97 \text{ kPa}$	$P_s = \text{Saturated}$
	$t_g \text{ (min)}$	$t_g \text{ (min)}$	$t_g \text{ (min)}$
100	35	41	30
110	34	35	15
120	27	31	8
130	24	23	6
140	22	18	4

As expected, from Table 3.1 it can be seen that the environmental temperature influences the gelation time of the resin. As the temperature of the experiment increases the time to gelation decreases. It is obvious that this behavior is due to the greater thermal energy supplied to the system as the temperature at which the experiment is

performed is increased. In addition, it can be observed for the temperature range 100 - 130 °C, an increase in the amount of moisture present in the environment (at not saturated conditions) results in an increase in time to gelation. This effect is probably a result of a slower rate of solvent water loss and thus a greater activation energy for polymerization. For 140°C it was found that the amount of moisture in the environment does not affect the gelation time of the resin. This unexpected result could be explained if it is considered that at this temperature level the thermal energy given to the system is high enough to overshadow the slower rate of solvent water loss due to the presence of moisture.

Table 3.1 shows that the introduction of saturated water vapor sharply decreased the gelation time when compared to the other environmental conditions. This is because at saturated conditions there is a larger heat transfer coefficient and also a higher adhesive temperature allowing the water to evaporate at a higher rate. These phenomenon can be seen clearly in Figure 3.6.

From the same figure it is found that the residual ion viscosity is affected by the water vapor environment. The higher the water vapor pressure the lower the residual ion viscosity. This behavior is probably due to some water trapped into the resin network which is acting as a plasticizer. Thus, a higher ion viscosity could perhaps be suggesting a higher level of cross-linking in the final adhesive network structure.

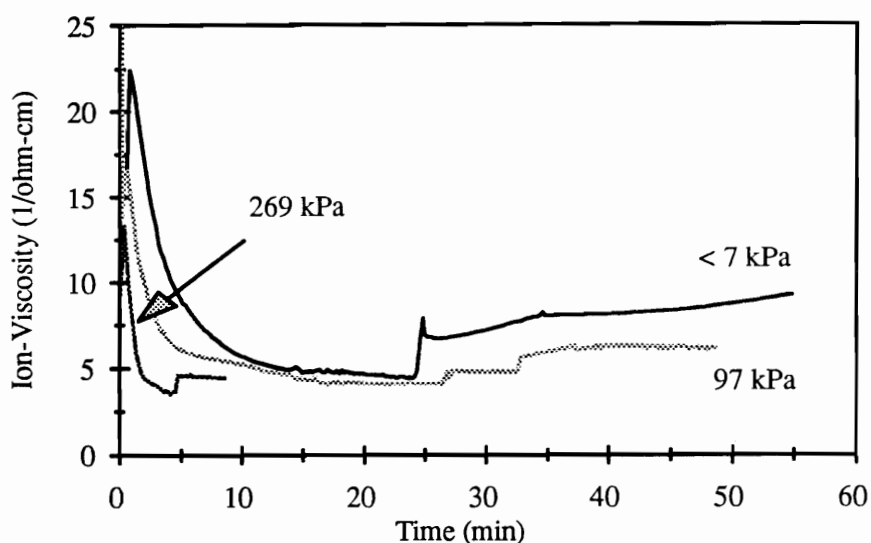


Figure 3.6 Residual ion viscosity as affected by water vapor pressure (130 °C)

Table 3.2 provides summary statistics for the gelation time measured for each combination of water vapor pressure and temperature. It can be observed that the coefficient of variation varied from 13.99 to 54.31 %. This variation is probably a result of different adhesive temperature profiles at the same environmental temperature condition. To compensate for the different temperature profiles, the gel time was adjusted. Time zero was set equal to the time at which the temperature of the adhesive reached 60 °C. This temperature was chosen based on the information given by a differential scanning calorimetry scan of the resin which shows that the polymerization reaction has not yet started. After performing the statistical analysis on the adjusted results it was found that the different adhesive temperature profiles did not affect the

Table 3.2 Summary statistics for the gel time

T (°C)	p _v (kPa)	t _{g,avg} (min)	σ _x	COV (%)
100	< 7	35	4.08	34.14
	97	41	2.49	24.64
	97 sat	30	0.82	16.53
110	< 7	34	0.82	15.53
	97	35	2.87	28.64
	138	15	1.25	28.87
120	< 7	27	1.25	21.52
	97	31	2.87	30.43
	200	8	0.82	32.02
130	< 7	24	0.47	13.99
	97	23	1.25	23.31
	269	6	0.47	27.99
140	< 7	22	0.47	14.62
	97	18	0.47	16.16
	352	4	1.18	54.31

σ_x : Standard deviation
COV : Coefficient of variation

variability of the gel time. Thus, physical limitations of the equipment and slight inconsistencies due to human error could be the source of this variability. It is clear that an increase in the number of replications for each condition is needed in order to decrease the variation in the experimental results.

A one way ANOVA model comparing the average gel time by the water vapor pressure level determined that significant differences existed between water vapor pressures at all temperatures ($p < 0.05$). Subsequent multiple comparisons by Tukey's honest significant difference (HSD) method ($\alpha = 0.05$) revealed a significant difference between atmospheric conditions ($p_v < 7$ kPa) and saturated conditions at all temperatures. For 120 and 140 °C it was found that there are also significant differences between an atmospheric and a complete water vapor (97 kPa) environment.

Gel Time Measurements

Gel time experiments, as measured by viscosity change, were carried out to provide comparative results with the microdielectric technique.

Figure 3.7 shows the variation of the angular rate of rotation and the temperature of the adhesive with time under a low humidity environment. It can be observed that the angular rate of rotation is constant till the gel point, then decreases. During the time before the gel point the molecular weight of the resin is too low to provide sufficient resistance for detection by the stirring mechanism. Once the gel point has been reached the molecular weight is so high that the resistance causes the stirring mechanism to stop. Thus, gelation time was defined as the point where the rotation stopped. The experimental results obtained using this technique at different water vapor conditions are shown in Appendix B.

Table 3.3 presents the values of gelation time obtained under different environmental conditions. It is observed that this technique gives similar trends to

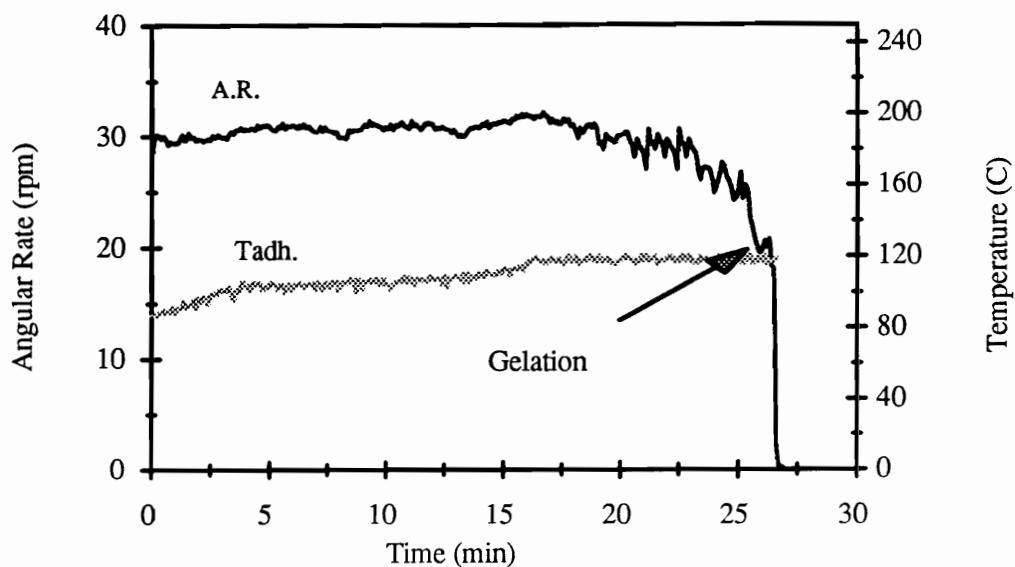


Figure 3.7 Experimental results given by the gel time measurement technique (< 7 kPa, 130 °C)

those obtained by dielectric analysis.

When comparing the actual values for gelation it was found that the results given by the gel time technique are approximately 5 minutes higher than those given by the DEA. The two techniques probe different material properties, thus the gel time measured is method-dependent. In the dielectric experiment, molecules and ionic species interact with an electric field with polar groups such as -OH, providing a local, sensitive indicator to observe relaxation characteristics. In the gel time technique the molecules are interacting with a mechanical stress.

Table 3.3 Gelation time from gel time measurements

T (°C)	$p_v < 7 \text{ kPa}$	$p_v = 97 \text{ kPa}$	$P_s = \text{Saturated}$
	$t_g \text{ (min)}$	$t_g \text{ (min)}$	$t_g \text{ (min)}$
100	38	47	25
110	33	33	17
120	28	30	11
130	26	23	7
140	16	20	5

As discussed previously, this technique was used to gather additional data about the rate of cure of the resin and, therefore, only one experiment for each condition was carried out. Thus, statistical analysis could not be performed.

Partial Time-Temperature-Transformation (TTT) Diagram

The TTT diagram has been shown to be an efficient form of describing the temperature dependent thermosetting network formation on the basis of the macroscopic observable parameters, gelation and vitrification (14, 15). On a molecular level gelation is defined as the incipient occurrence of one molecule of infinite molecular weight. Gelation occurs at a defined extent of reaction and does not change the kinetics of the reaction (16). Thus it can be observed only by methods based on changes of mechanical,

electrical and viscoelastic properties.

Relying on the information given by the dielectric analysis, gelation times were used to form part of the TTT-diagram of an aqueous phenol formaldehyde adhesive system under an atmospheric ($p_v < 7$ kPa) and a complete water vapor ($p_v = 97$ kPa) environment. These partial TTT-diagrams are presented in figures 3.8 and 3.9. The Y-axis is the environmental temperature at which the resin was cured isothermally and not the measured adhesive temperature. The glass transition of the uncured phenolic resin was obtained using a Perkin Elmer DSC-4 and the temperature scan is shown in Appendix C.

Difficulties were experienced in attempting to define the glass transition of the fully cured resin. Differential scanning calorimetry and thermal mechanical analysis (expansion and penetration modes) were unsuccessful in determining this temperature. It is assumed that the high degree of cross-linking of the fully cured resin made impossible the use of these two techniques. Dynamic mechanical thermal analysis scans were not performed because it was impossible to prepare suitable samples from the partially cured phenolic resins.

From Figures 3.8 and 3.9 it can be observed that there is a displacement to the left in gelation time when working at atmospheric conditions ($p_v < 7$ kPa) at temperatures below 130 °C. As it was previously discussed, this behavior is explained by the higher rate of solvent loss under the low water vapor pressure conditions. Above 130 °C the thermal energy supplied to the system is high enough to overshadow the slower rate of solvent water loss due to the presence of moisture. It is interesting to point out that the

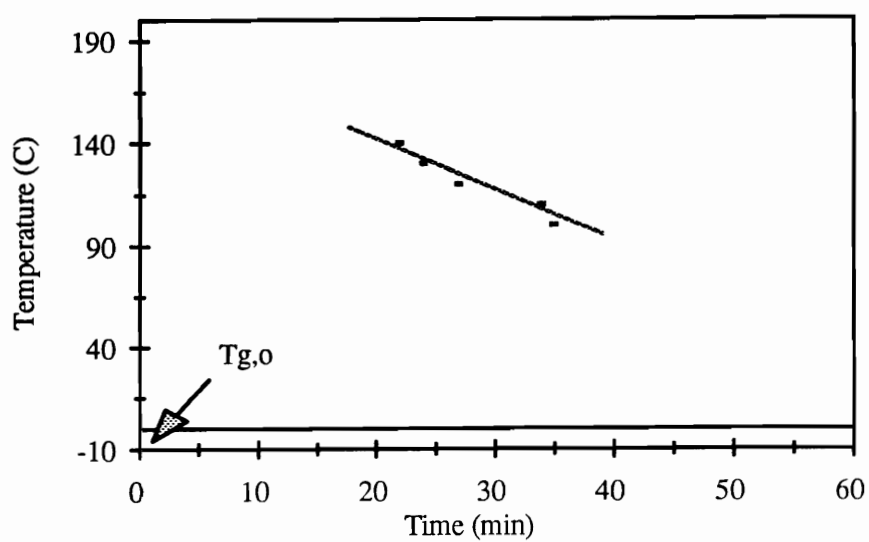


Figure 3.8 Partial TTT-diagram for phenol formaldehyde at $p_v < 7$ kPa (gelation curve)

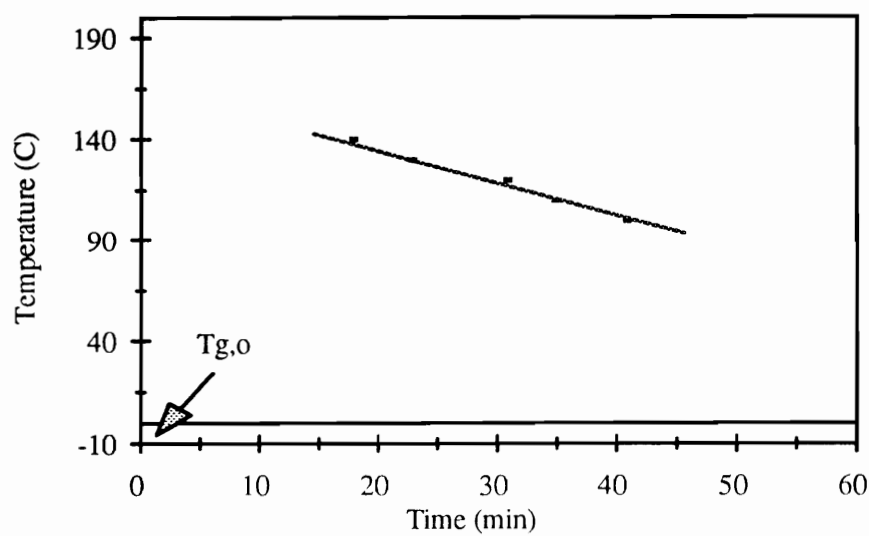


Figure 3.9 Partial TTT-diagram for phenol formaldehyde at $p_v = 97$ kPa (gelation curve)

slope of the curve of the environment temperature versus gelation time for the atmospheric condition is greater than the slope for a complete water vapor environment.

It is important to mention that these diagrams are specific to this particular phenolic system and that there is a great amount of work still ahead in order to have a complete cure diagram. Nevertheless, this is the first step in the search of that diagram, which would permit time-temperature paths of cure to be identified. Thus, gelation, vitrification, and phase separation could be controlled, and consequently give rise to predictable properties of the resin matrix.

Conclusions

Microdielectric spectroscopy and gel time measurements are effective techniques for studying in situ the onset of gelation of phenol formaldehyde adhesive systems in pressurized environments.

The times to gelation as measured by the gel time measurement technique correlate fairly well with times as measured by microdielectric spectroscopy, even though these methods probe different material properties.

From the experimental data given by microdielectric spectroscopy a part of a Time-Temperature-Transformation (TTT) diagram for phenolic resins was developed. This partial TTT diagram was obtained for different water vapor environments.

The cure kinetics of aqueous phenol formaldehyde is affected by temperature and water vapor pressure. As the temperature of the experiment increases, the time to gelation decreases, and an increase in the amount of moisture present in the environment results

in an increase in the time to gelation.

Additional research is needed to better understand the cure behavior of phenolic resins under different water vapor environments. The TTT diagram must be completed and an understanding of the molecular character of the resin as affected by the water vapor environment is essential.

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CHAPTER 4

NETWORK CHARACTERIZATION OF A RESOL RESIN CURED UNDER DIFFERENT WATER VAPOR ENVIRONMENTS.

Introduction

Traditional wood composite products, such as structural plywood, particleboard, fiberboard, and oriented strand board, utilize urea or phenol formaldehyde adhesive systems (usually aqueous). Even these inexpensive adhesives can represent 50 % or more of the raw material cost in these wood composites. As these composites and other products evolve and compete in the market place, adhesive bond performance must improve.

Thermosetting adhesives are exposed to fluctuating temperature and moisture conditions within composite materials being hot pressed. These variables affect the kinetics of polymerization and associated bond-strength development, in turn, influencing the time required for processing. Thus, a quantitative understanding is needed of the responsiveness of the adhesives to the conditions that develop within composites during pressing.

In the previous chapter it has been shown that the water vapor pressure is affecting the properties of the cured resin. It is believed that there is some water trapped in the resin network and acts as a plasticizer. This could affect parameters such as cross-link density (1), and the degree of stress locked into the network. Furthermore, this phenomenon may control the behavior of the thermoset in the glassy region, where

properties such as the linear coefficient of thermal expansion, water absorption, and elastic modulus are affected (2).

The objective of this paper is to determine if water vapor pressure influences the chemical structure and morphology of cured phenol-formaldehyde resin.

Glass Transition Temperature

The glass transition temperature (T_g) is defined as the temperature at the onset of large-scale motion of molecular chain segments. At very low temperatures, near the absolute zero, chain atoms undergo only low-amplitude vibratory motion around fixed positions. As the temperature is raised, both the amplitude and the cooperative nature of these vibrations among neighboring atoms increase, until at a well-defined transition at temperature T_g , segmental motion becomes possible, and the material becomes rubbery. Above T_g , the chain segments can undergo cooperative rotational, translational, and diffusional motions, and as the temperature is raised the material behaves like a high viscous liquid (7).

The glass transition temperature of thermosetting polymers determines an upper temperature limit for the use of the cured polymer. The T_g also influences the chemorheology, development of internal stresses and the onset of the diffusion control regime during the isothermal cure of a thermoset (3-6, 8-10).

When cross-links are introduced into a polymer, the density of the sample is increased proportionally. As the density increases, the molecular motion in the sample is restricted and T_g increases. T_g is found to increase linearly with the number of cross-

links.

Cross-link Density

The cross-link density is defined as the number of moles of elastically effective cross-links per unit volume of polymer (11). Solvent swell is a traditional measure of the cross-link density. Swelling is accompanied by an increase in the volume of the polymer as it imbibes the solvent. It is usual to assume, consistent with the Flory-Huggins theory of the thermodynamics of polymer solutions (12), that this mixing occurs without change in the total volume of the system. As a result it is possible to write an expression for the volume V_{∞} of the swollen polymer in terms of the original weight $\mathfrak{w}_0$ and swollen weight $\mathfrak{w}_{\infty}$ and the densities ρ_p and ρ_s of the polymer and solvent, respectively:

$$V_{\infty} = \frac{\mathfrak{w}_0}{\rho_p} + \frac{(\mathfrak{w}_{\infty} - \mathfrak{w}_0)}{\rho_s} \quad (4.1)$$

As the network is swollen by absorption of solvent, the chains between network junctions are required to assume elongated configurations, and a force akin to the elastic retractive force in rubber consequently develops in opposition to the swelling process. As swelling proceeds, this force increases and the diluting force decreases. Ultimately, a state of equilibrium swelling is reached in which these two forces are in balance. This condition is defined by the concentration of polymer in the swollen polymer-solvent mixture at equilibrium. Calling this concentration c , it is possible to write following Flory-Rehner equation (13):

$$-\left[\ln(1-c) + c + \chi c^2\right] = \left(V_s \frac{\rho_p}{M_c}\right) \left(c^{1/3} - \frac{c}{2}\right) \quad (4.2)$$

where the left-hand side represents the lowering of the chemical potential due to mixing and the right-hand side its increase from the elastic reaction of the network. The equation 4.2 as written here applies to a perfect network (no dangling chain ends) for which the molecular weight per cross-linked unit is M_c . The quantity V_s is the molar volume of the solvent, and χ is the polymer-solvent interaction parameter of the Flory-Huggins theory. This equation can readily be solved for M_c :

$$M_c = \frac{-V_s \rho_p \left(c^{1/3} - \frac{c}{2}\right)}{\ln(1-c) + c + \chi c^2} \quad (4.3)$$

The concentration c at equilibrium is given by

$$c = \frac{\bar{w}_0}{\rho_p V_\infty} \quad (4.4)$$

The polymer-solvent interaction parameter χ can be obtained from the temperature dependency of the swelling volume as follows:

$$\frac{d \ln c}{d \ln T} = \frac{-3\chi(1-c)}{5(1-\chi)} \quad (4.5)$$

The cross-link density ρ_c is given by:

$$\rho_c = \frac{\rho_p N_{Av}}{M_c} \quad (4.6)$$

where N_{Av} is the number of Avogadro.

Materials and Methods

Materials

Phenol-formaldehyde resin samples cured under five different temperature conditions (100-140 °C) and three water vapor environments (< 7 kPa, 97 kPa, and saturated conditions) were used. The curing conditions and the methodology used to cure the resin are explained in Chapter 3. After the curing process, the cured resin samples were stored at subambient conditions. Freezing the samples stopped the polymerization reaction allowing the properties of the resin network to remain unaffected.

Methods

Thermomechanical Analysis

A Perkin-Elmer TMS-325 thermomechanical analyzer was used to determine the glass transition temperature of the resin networks (Figure 4.1). Thermomechanical analysis is a technique in which the deformation of a substance is measured under nonoscillatory load as a function of temperature as the substance is subjected to a controlled temperature program. After preliminary trials it was found that the sample penetration probe was more suitable to carry out the thermal analysis experiments for these particular cured-resin samples than the thermal expansion probe. Thus, all the

thermal analysis results presented in this paper were obtained using the penetration mode. The samples were prepared using a razor blade. Smooth surfaces were able to be obtained and the average thickness of the samples was 0.08 cm. The temperature range covered was -130 to 200 °C and a 10 g. load was used. Liquid nitrogen was used to obtain subambient conditions and compressed nitrogen was used as a gas purge. The samples were freeze-dried for 24 hours at 1.7 kPa and -100°C, and then placed on the platform of the sample tube and heated at a rate of 2.5 °C/min.. Sample temperature was monitored by a thermocouple placed inside the furnace directly adjacent to the sample. Three replications of each treatment combination were made resulting in a total of 45 thermal analysis experiments.

Swelling Tests

The effective cross-link density of the phenol formaldehyde resin networks was determined by the Flory-Rehner method (13) explained earlier in this chapter. Prior to the swelling test the resin samples were freed from soluble materials by extraction with methanol for 24 hours. A subsequent vacuum drying of the samples at room temperature for 18 hours was carried out. The resin samples were weighed dry and each one was placed in a 20 cubic centimeter vial filled up with water at 75 °C. The average weight of the resin samples was 0.05 g.. The vials with the samples were immersed in a water bath maintained at 75 °C. The resin networks were swollen for five days. The samples were then removed from the solvent , quickly blotted dry of excess water on the surface and weighed.

The density of the cured phenol-formaldehyde resin was obtained by the use of the displaced volume technique. Two resin samples of known weights cured under different water vapor conditions were immersed in toluene at 22 °C. The volume displaced for the samples was obtained from gravimetric measurements. Three replications for each treatment were carried out. The average density of the six experiments performed was considered as the density of the polymer.

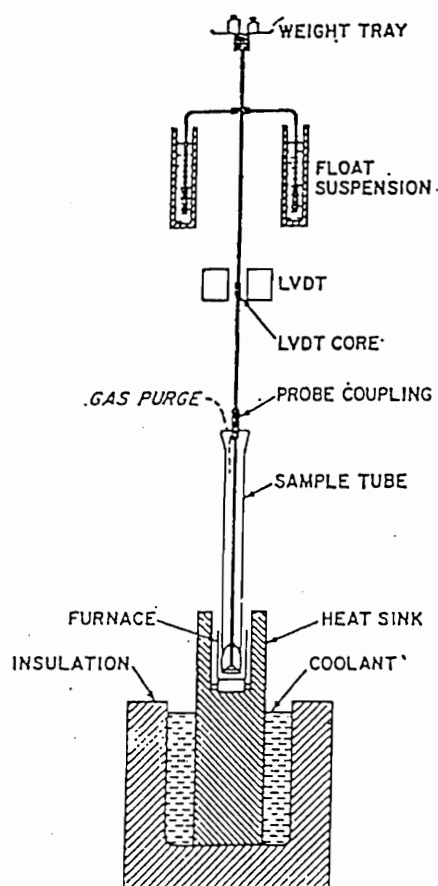


Figure 4.1 Thermomechanical analyzer apparatus.

In order to determine the polymer-solvent interaction parameter χ for the cured-phenol-formaldehyde resin-water system, additional swelling tests were carried out at 25, 30, 40, 50, and 69 °C.

Scanning Electron Microscopy (SEM)

In order to have complementary information about the cured resin networks electron microscopy scans (AMRAY model 1810) were performed for samples cured at three different water vapor conditions. The samples were immersed in liquid nitrogen and then they were broken. The surface of the samples broken under this condition was exposed to the electron beam. All samples were coated with gold-palladium (60:40 %).

Results and Discussion

TMA Analysis

A typical TMA trace plots the change in number of counts versus temperature. Where the number of counts is an arbitrary unit proportional to the vertical motion of the probe. In order to make the data more readily interpretable the number of counts were converted to percent of the thickness of the sample. The 100 % thickness was defined as the counts recorded with the probe just touching the top of the sample at the beginning of the thermal scan. A complete set of scan results are contained in Appendix D.

Figure 4.2 shows how the chart was used to obtain the glass transition temperature. This temperature was determined by extrapolation of the base line and the displaced penetration curve which shows the onset of probe penetration (14, 15).

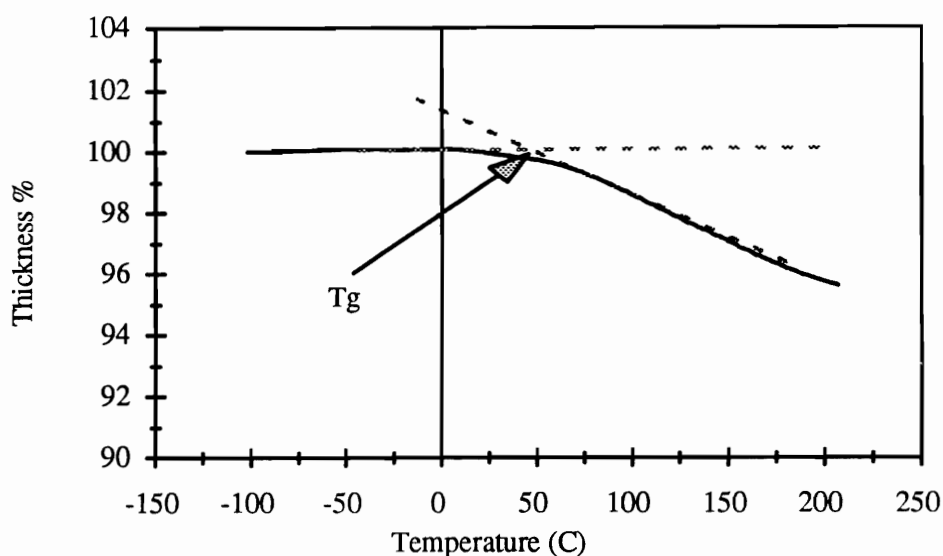


Figure 4.2 TMA chart, 97 kPa, 130 °C. Glass transition determination

The glass transition temperatures of the resin samples cured under different conditions are presented in Table 4.1. It is important to recall that these T_g 's corresponds to the average value of three thermal scans obtained from different cure runs.

As indicated in Table 4.1, higher cure temperatures produced resin networks with higher glass transition temperatures. This result was expected considering that a higher cure temperature is necessary to accelerate the condensation reaction of phenol formaldehyde, thereby increasing the degree of cross-linking of the cured polymeric network. It is interesting to notice that for atmospheric conditions (< 7 kPa) even though T_g generally increases with temperature, there is not a consistent trend. It is believed that this phenomenon is due to variability in the degree of cure within the resin sample as a

result of nonuniform conditions at different positions in the specimen container. The reason why this behavior may have occurred only under atmospheric conditions has not been identified. On the other hand, at a constant cure temperature, the higher the water vapor pressure the lower the glass transition temperature of the network. This behavior is probably due to a lower cross-link density of the resin network. Several of the phenol formaldehyde reaction pathways are condensation reactions and water will participate in the equilibrium of each of the possible condensation steps. Thus, the presence of water or water vapor will affect the position of condensation equilibria and therefore the rate of any condensation reaction.

From the same table it can be observed that the coefficient of variation ranged from 4.95 to 40.71 %. As mentioned earlier, this variation could be a result of nonuniform conditions at different positions in the specimen container.

In Figure 4.3 it is shown how the water vapor environment affects the sample penetration. The higher the water vapor pressure used during the curing process the higher the probe penetration. In other words, the polymeric network is imposing less resistance to the probe. This behavior is suggesting that as the water vapor conditions are increased the molecular mobility of the resin network is also increased. Thus, sample penetration and glass transition results are in agreement with the results reported in Chapter 3 using microdielectric spectroscopy, corroborating the assumption that some water is trapped into the resin network affecting the degree of cross-linking.

Table 4.1 T_g determined by TMA

T (°C)	p_v (kPa)	T_g (°C)	COV (%)
100	< 7	76	12.39
	97	34	18.03
	97 sat	23	6.17
110	< 7	73	31.36
	97	48	27.85
	138	38	5.32
120	< 7	110	7.51
	97	63	5.65
	200	42	10.83
130	< 7	98	12.83
	97	63	24.54
	269	51	26.10
140	< 7	111	4.95
	97	90	12.58
	352	58	40.71

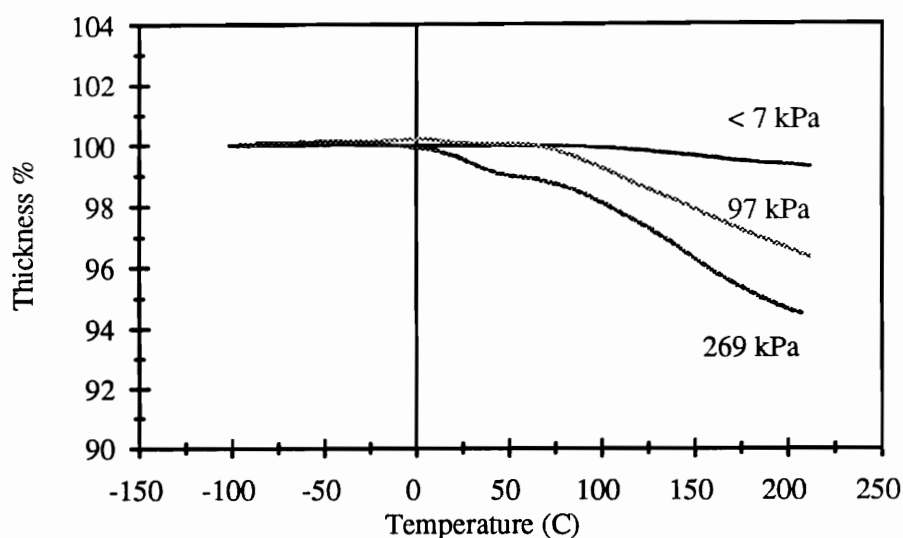


Figure 4.3 Sample penetration using TMA at 130 °C.

During preliminary TMA trials, wet (as the resin was stored after curing) and freeze-dried resin samples were scanned. It was found that the spectra showed significant differences (Figure 4.4). The freeze-dried sample exhibits a typical thermomechanical spectrum. The wet sample exhibits what appears to be a second transition in the range of 75 to 100 °C. A possible explanation for this behavior is that the cured resin has a porous structure. In this temperature range the material is softening and condensed water is evaporating into the voids and expanding the network. Reed (16) found the same type of behavior when working with epoxy/glass composites. The author pointed out that this behavior was indicating a change in the coefficient of thermal expansion of the sample as the cross-link density was changing.

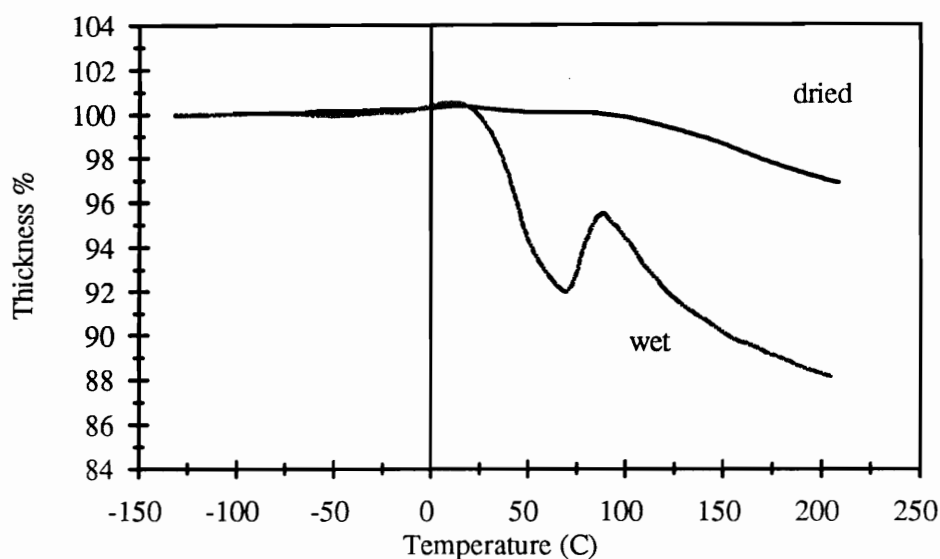


Figure 4.4 TMA scan, 97 kPa and 140 °C. Wet and freeze-dried samples

In order to corroborate the assumption that the resin network had a porous structure, electron microscopy scans were performed for wet and freeze-dried resin samples. Figures 4.5, 4.6 and 4.7 show the SEM photomicrographs for a resin cured under different water vapor environments at 140 °C. The three resin samples exhibit a highly porous structure. It is also observed that there are considerable structural differences in the polymeric network depending on the curing conditions. Thus, it is reasonable to expect that the strength properties of the cured resin are going to be affected by the environmental conditions at which the curing process is carried out. It is obvious that the water vapor is playing a major role in the final structure of the resin network. At atmospheric conditions the network appears to have many fractures due to curing

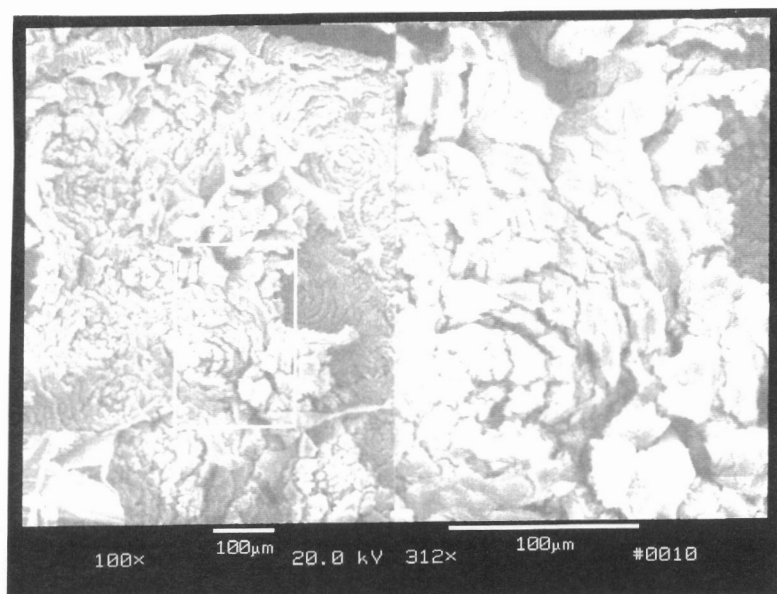


Figure 4.5 SEM of a resin cured at atmospheric conditions (< 7 kPa) and 140 °C.

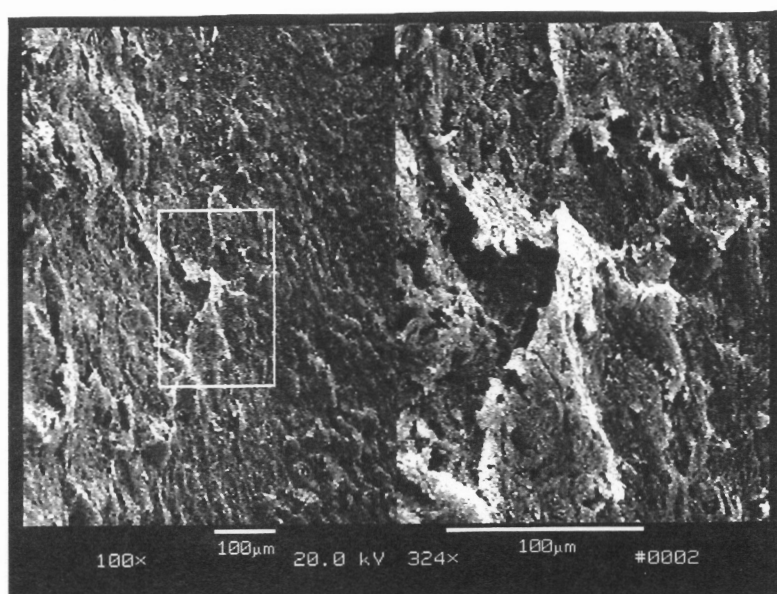


Figure 4.6 SEM of a resin cured at 97 kPa water vapor pressure and 140 °C.

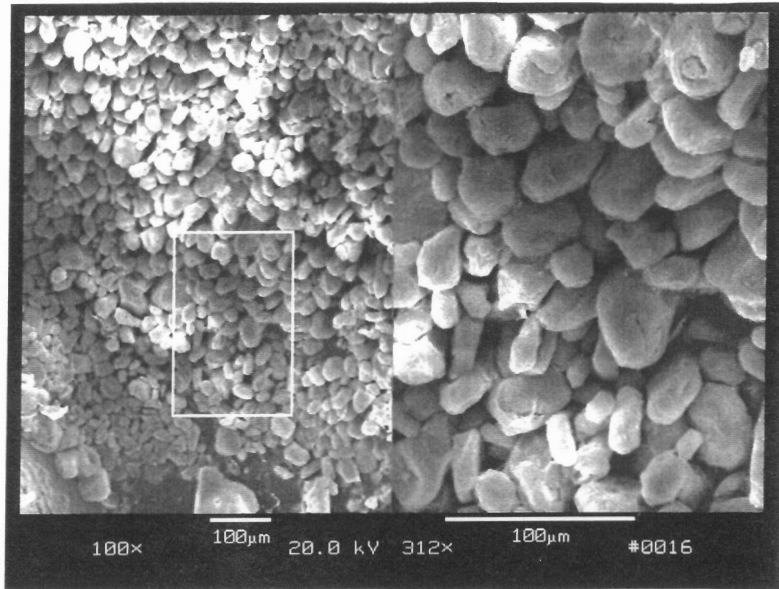


Figure 4.7 SEM of a resin cured at saturated conditions (352 kPa) and 140 °C.

stresses and at 97 kPa complete water vapor environment the network is porous, but slightly fractured. On the other hand, at saturated conditions the network is porous and not fractured. It appears to have coalesced into separate domains in the presence of a large amount of water. Another possible explanation is that the network experiences phase separation to form a microgel. Thus, Figure 4.7 shows differences in microgel formation.

Figures 4.8, 4.9 and 4.10 show the SEM photomicrographs for the freeze-dried resin samples. Surprisingly, a relatively smooth and nonporous surface is observed. A possible reason explaining the significant differences between freeze-dried and non freeze-dried surfaces has not been identified.

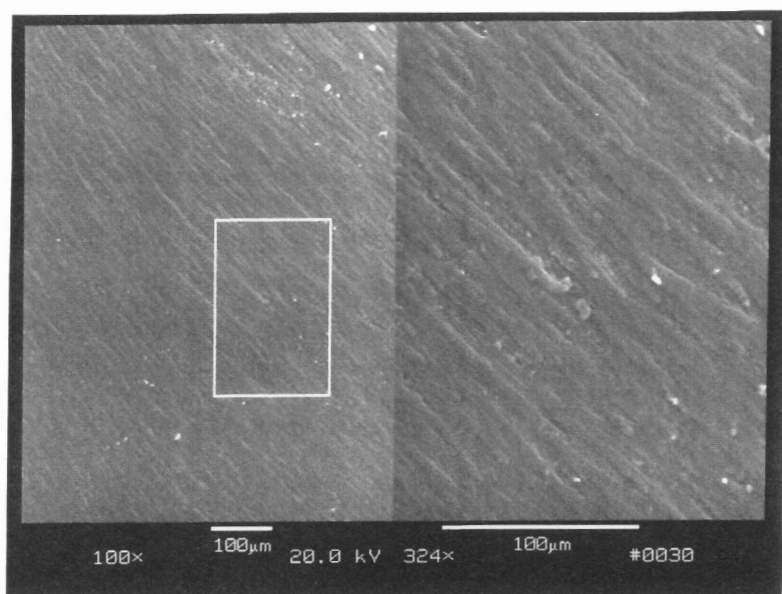


Figure 4.8 SEM of a freeze-dried resin cured at < 7 kPa water vapor pressure and 140 °C.

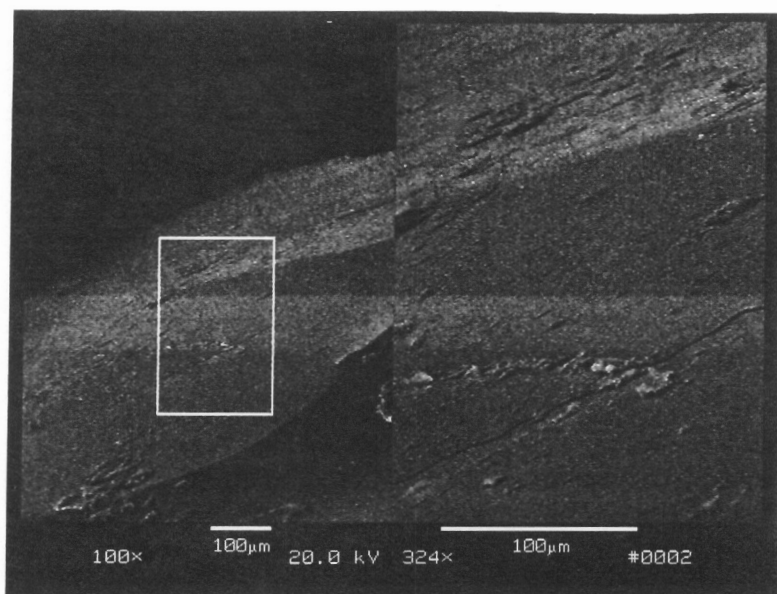


Figure 4.9 SEM of a freeze-dried resin cured at 97 kPa water vapor pressure and 140 °C.

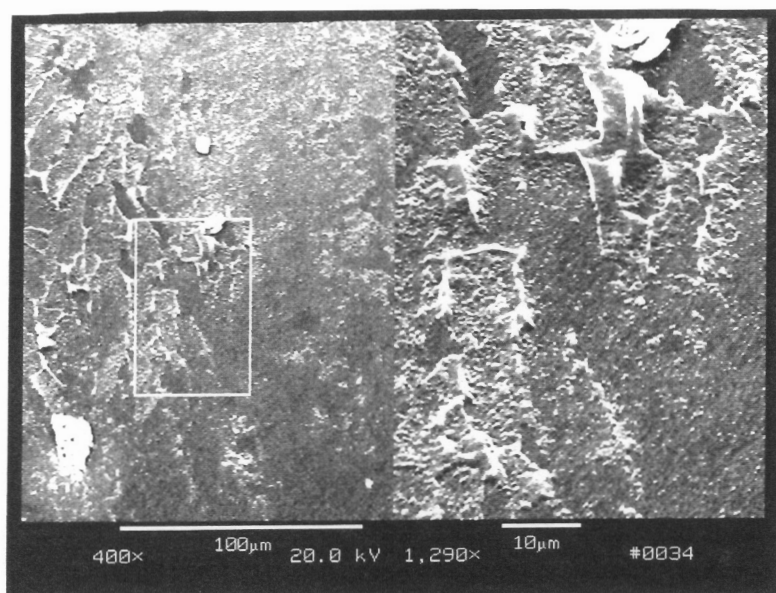


Figure 4.10 SEM of a freeze-dried resin cured at saturated conditions (352 kPa) and 140 °C.

Swelling Tests

In order to calculate the molecular weight between cross-links (M_c) and the cross-link density per unit volume of polymer (ρ_c) the value for the polymer-solvent interaction parameter must be determined. Preliminary trials using 1,4-dioxane, 1,2-dichlorobenzene, methanol, toluene and water were performed to define a suitable swelling solvent for the polymer network. It was found that water was the best swelling solvent for this system. This solvent was able to depress the T_g of the resin network when working at 75 °C ensuring that the swelling test was carried out in the rubbery region. It must be recalled that the Flory-Huggins theory is based on rubber elasticity so the swelling tests must be

carried out above the glass transition temperature of the network. As it was mentioned in the methods section of this chapter, all the low molecular weight material of the polymer samples were extracted. The presence of any uncross-linked materials in the polymer network, which may dissolve and change the concentration, can be a source of error. The χ value for the cured-phenol formaldehyde-water system was calculated according to equation 4.5. The logarithmic variation of the concentration at equilibrium versus temperature was obtained from Figure 4.11. A χ value of 0.76 was obtained.

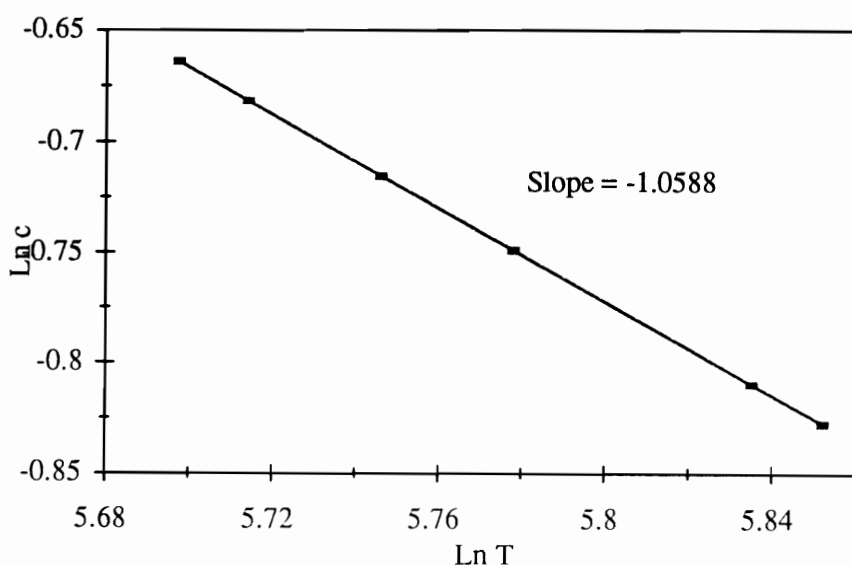


Figure 4.11 $d(\ln c) / d(\ln T)$ value for the determination of the χ parameter.

It is assumed that the χ parameter is concentration independent and that any possible specific solvent-polymer interactions which might lead to orientation of the solvent molecules in the vicinity of the polymer chain are negligible.

Values for the χ parameter for different systems have been reported in the

literature (17,18) in a range from -0.28 to 1.3. No information about the value of this parameter for phenolic systems was found. Thus, the value of 0.76 for this system is within the range of χ values reported by others for thermosetting systems.

Table 4.2 shows the concentration at equilibrium, cross-link density, and molecular weight between cross-linked points for the resin cured under different conditions. In general the cross-link density increases with temperature. At a given temperature it is observed that the cross-link density decreases as the water vapor pressure increases. This result is in agreement with the results obtained using TMA and those presented in Chapter 3 using microdielectric spectroscopy. Thus, it is possible to confirm the hypothesis that the water vapor pressure is affecting the degree of cross-linking of phenol formaldehyde. It is also clear that effectively there is some water in the network structure acting as a plasticizer during cure. The missing values reported in Table 4.2 are a consequence of the high degree of swelling reached for those samples. When applying equation 4.3 a negative value for the molecular weight between cross-linked units was found. Flory (12) reported that at low degrees of cross-linking, M_c values of 10,000 or more, the term $c/2$ of equation 4.3 can be neglected. To a similar approximation higher terms in the series expansion of $\ln(1 - c)$ may be neglected giving the following result for the swelling equilibrium equation:

$$M_c = \frac{V_s \rho_p}{C^{5/3} \left(\frac{1}{2} - \chi \right)} \quad (4.7)$$

Equation 4.7 offer a clear insight into the dependence of the molecular weight between cross-links on the quality of the solvent as expressed by χ , and on the

Table 4.2 Cross-link density and molecular weight between cross-linked points

T (°C)	P _v (kPa)	C _{avg} *	M _c (g/mole)	ρ _c (molec./cc)
100	< 7	0.5200	1475	5.38 x 10 ²⁰
	97	0.5119	1982	4.01 x 10 ²⁰
	97 sat	0.3520	N/A	N/A
110	< 7	0.5209	1432	5.54 x 10 ²⁰
	97	0.5023	3163	2.51 x 10 ²⁰
	138	0.4551	N/A	N/A
120	< 7	0.6698	134	5.93 x 10 ²¹
	97	0.5475	727	1.09 x 10 ²¹
	200	0.4855	35953	2.21 x 10 ¹⁹
130	< 7	0.5912	345	2.30 x 10 ²¹
	97	0.5461	749	1.06 x 10 ²¹
	269	0.4921	7401	1.07 x 10 ²⁰
140	< 7	0.6874	112	7.10 x 10 ²¹
	97	0.6096	268	2.96 x 10 ²¹
	352	0.5226	1358	5.85 x 10 ²⁰

* Average of three replicates

N/A Not available

equilibrium concentration. Therefore, for this equation to be used, the χ parameter should be lower than 0.5. Thus, the negative values obtained for high degree of swelling are a consequence of the experimental and theoretical difficulties encountered with the Flory-Huggins thermodynamic theory, upon which the development of equation 4.3 is based. Besides the two limitations already explained for the χ parameter, it must be considered that the theory assumed that the flexibility of the chain is unaltered on passing into the solution from the solid state, and therefore, neglects any contribution from continual flexing of the chain in solution which will contribute to the non-combinatorial or excess entropy of mixing.

As mentioned previously the concentration at equilibrium was determined as the average of three replicates. Table 4.3 shows the coefficients of variation for the concentration at equilibrium at each condition. It can be observed that the coefficient of variation ranged from 4.52 to 18.45 %. In general the variability is less than 10 %. Then, it is clear that the value 18.45 found for 97 kPa and 140 °C is an outlier. Thus, the values of concentration lie close to their mean and it can be concluded that no significant experimental errors were affecting the swelling measurements.

Figure 4.12 shows the relationship between the T_g of the resin and the network density expressed in terms of the molecular weight of chains between cross-links for a given temperature. It can be seen that the glass transition of the network decreases as the molecular weight between cross-links is increased. This trend is consistent with that expected for thermosetting polymers since, as the network density is lowered, molecular motion within the sample is much less restricted and the T_g is consequently lowered.

Table 4.3 Coefficient of variation for concentration data

T (°C)	p _v (kPa)	COV (%)
100	< 7	10.39
	97	5.13
	97 sat	N/A
110	< 7	6.72
	97	6.30
	138	N/A
120	< 7	10.70
	97	10.90
	200	8.08
130	< 7	4.92
	97	8.92
	269	8.07
140	< 7	4.52
	97	18.45
	352	9.91

N/A Not available

COV: Coefficient of variation

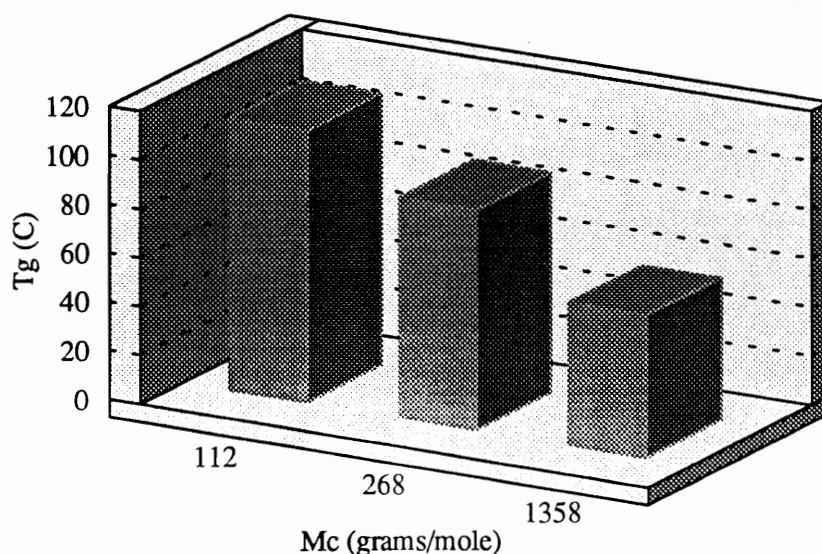


Figure 4.12 Relationship between T_g and M_c

To confirm that the absorption of water by the resin was actually swelling the network and not only filling the pores of the sample two video image analysis experiments were carried out. The image of the same sample before and after swelling were captured using a Zeiss D-7082 Axioskop microscope connected to a monitor using a DAGE-MTI CCD 72 television camera. The samples were measured using a 4.0x objective, which corresponds to 135x on the image monitor. This magnification was used because it presented the largest field of view measurement.

Figures 4.13, 4.14, 4.15 and 4.16 show that there is a considerable change in the morphology of the network after swelling with water. This confirms that water is swelling the network and that the chains between network junctions are assuming elongated configurations.

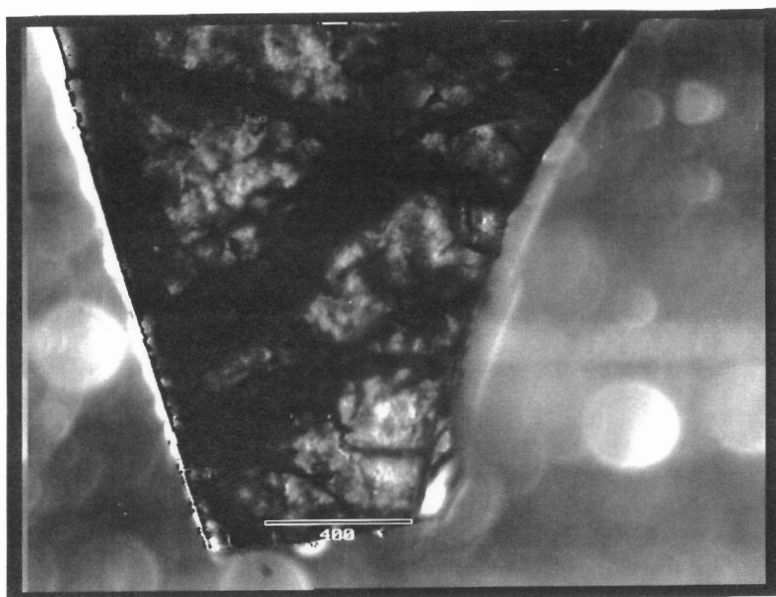


Figure 4.13 Resin sample cured at 97 kPa and 120 °C prior to swelling.

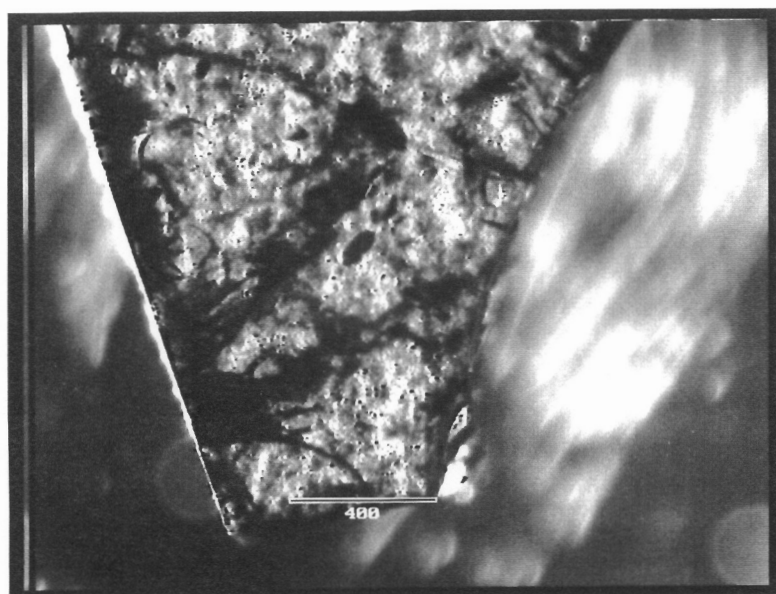


Figure 4.14 Resin sample cured at 97 kPa and 120 °C after swelling.

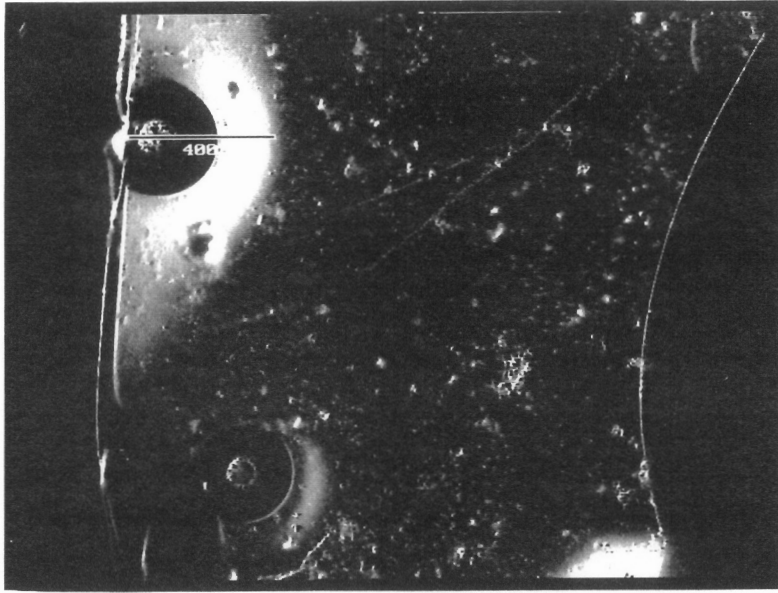


Figure 4.15 Resin sample cured at < 7 kPa and 140°C prior to swelling.

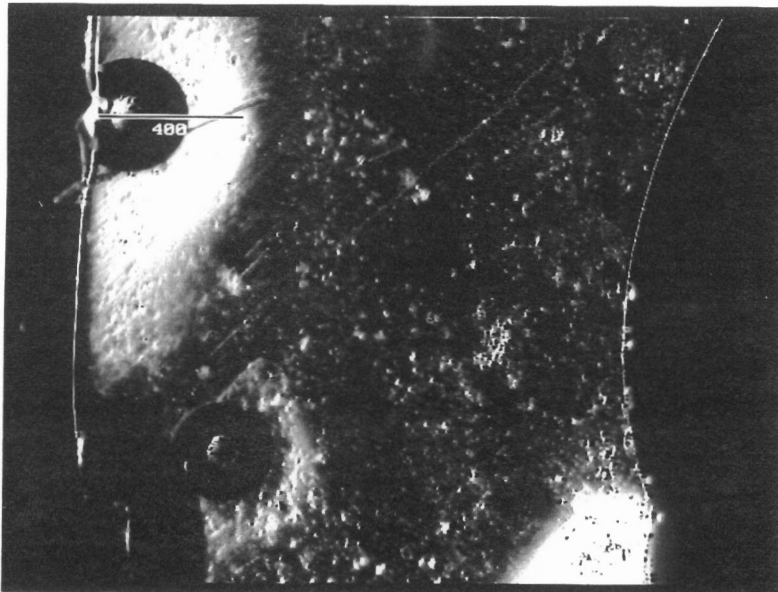


Figure 4.16 Resin sample cured at < 7 kPa and 140°C after swelling.

Conclusions

Thermomechanical analysis and swelling tests are effective techniques for studying the glass transition temperature, the cross-link density and the molecular weight between cross-links of a cured phenol formaldehyde thermosetting resin.

From the experimental data given by these techniques, it can be established that during the curing process under elevated water vapor pressures of a liquid phenol formaldehyde adhesive some water is trapped into the resin network and it is acting as a plasticizer. In addition, it can be established that water vapor environments affect considerably the molecular weight between cross-links and the cross-link density of the resin network.

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CHAPTER 5

MODELLING THE CURE KINETICS OF AQUEOUS PHENOL FORMALDEHYDE THERMOSETTING ADHESIVE. A THEORETICAL APPROACH.

Introduction

Phenol-formaldehyde is polymerized and processed in a single operation which involves the irreversible transformation of a resin with a low molecular weight into a network polymer. The cross-linking reaction is dependent upon the type of resin, the relative concentrations of the curing agent, the temperature and also upon the water vapor pressure.

Previous chapters have been shown that temperature and water vapor pressure are affecting the rate of the polymerization reaction, and therefore, the properties of the cured resin. Thus, it is of foremost importance to have a good knowledge of the way in which the interrelationship of these variables is affecting the process of cure.

Modelling the process of cure is of great interest either from a theoretical point of view or for practical and industrial applications. A model enables the user to evaluate the effect of each parameter on the process in a quantitative manner, however great their number, thus reducing the amount of experimentation. Simulating the process is necessary to determine the best operational conditions when the process of cure must be developed on a larger scale than the laboratory scale for which the model was tested. This information is of great concern, as the main objective in industry is to reduce the

price of the final material and to improve its quality, at the same time (1).

The objective of this study is to develop a theoretical model of the cure kinetics of aqueous phenol-formaldehyde thermosetting adhesive as a function of temperature and water vapor pressure.

Theoretical Model

It is the aim of any kinetic study to determine how a reaction proceeds. However the determination of reliable kinetic data for phenolic resin formation is complicated because the reaction conditions, including temperature, type and amount of catalyst, and mole ratio and polarity of the solvents exert a profound influence on the results obtained (2). Thus, modelling the process of cure is rather complex not only due to the interaction of all these variables but also for the selection of a kinetic equation of the overall cure reaction.

To the present, research on cure kinetics of phenol-formaldehyde has been done without considering how the evaporation of water is affecting the kinetic parameters. In the model that it is presented herein it is considered that there are two simultaneous processes occurring; the polymerization reaction of phenol-formaldehyde and the evaporation of water.

In order to simplify the model, it is assumed that the phenolic resin can be characterized as a di-substituted ortho-para-methylolphenol (o-p-HMP) system. This assumption is based in the fact that the para-position in phenol shows a slightly higher

relative reactivity towards formaldehyde than the ortho-position (electron density value) and that, even though o-HMP reacts at a higher rate to form o-o-HMP, the overall rate of formation of o-p-HMP from ortho-HMP and para-HMP is higher. Thus, the condensation polymerization reaction of phenol-formaldehyde is given by:

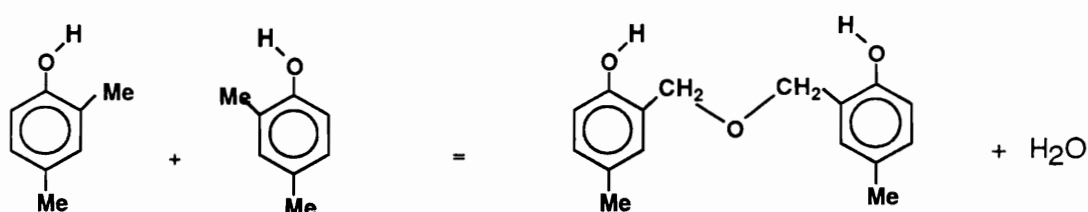


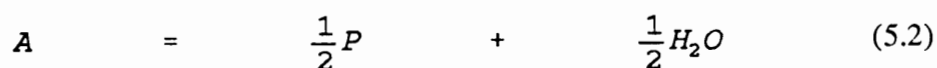
Figure 5.1 Polymerization reaction of phenol-formaldehyde

For convenience the polymerization reaction can be written as:



where A and P are the reactant and product respectively.

Rearranging equation 5.1 and defining initial and final conditions it can be written:



(initial) n_{A0} 0 n_{H0}

(reacting) $n_{A0}F$

(final) $n_{A0}(1-F)$ $0.5n_{A0}F$ $n_{H0} + 0.5n_{A0}F$

where;

n_{A0} : initial moles of reactant A

n_{H0} : initial moles of water in the system (control volume)

F : extent of conversion

$n_{A0}F$: moles of reactant A converted to products

n_A : moles of reactant A at any time

Determination of the Rate of the Reaction

The rate of the reaction is defined as the number of moles of component A reacting (disappearing) per unit time per unit volume (moles A/volume-time) (3):

$$-\Gamma_A = \frac{dC_A}{dt} \quad (5.3)$$

where C_A is the concentration of reactant A;

$$C_A = \frac{n_A}{V} \quad (5.4)$$

with V as the volume of the system (control volume). Replacing C_A in equation 5.3 ,

$$-\Gamma_A = \frac{d(\frac{n_A}{V})}{dt} = \frac{d(\frac{n_{A0}[1 - F]}{V})}{dt} \quad (5.5)$$

or

$$-\Gamma_A = n_{A0} \frac{d(\frac{1}{V})}{dt} - n_{A0} \frac{d(\frac{F}{V})}{dt} \quad (5.6)$$

but the control volume and the conversion are changing with time. Therefore;

$$\frac{d(\frac{1}{V})}{dt} = \frac{1}{V^2} \frac{dV}{dt} \quad (5.7)$$

and

$$\frac{d(\frac{F}{V})}{dt} = \frac{1}{V} \frac{dF}{dt} - \frac{F}{V^2} \frac{dV}{dt} \quad (5.8)$$

Replacing equations 5.7 and 5.8 in equation 5.6 and rearranging,

$$-\Gamma_A = \left[\frac{n_{A0}F}{V^2} - \frac{n_{A0}}{V^2} \right] \frac{dV}{dt} - \frac{n_{A0}}{V} \frac{dF}{dt} \quad (5.9)$$

The control volume is defined as the volume occupied by the resin solids and the solvent water. Thus, for the system presented in Chapter 3, the control volume corresponds to the volume occupied by the liquid resin in the specimen container housed inside the small reactor.

Molar Balance of Water

A molar balance on water at any instant in time, t , is given by:

$$\begin{array}{lll} \text{rate of} & & \text{rate of} & & \text{rate of flow} \\ \text{accumulation of water} & = & \text{generation by} & - & \text{of water out of the} \\ \text{within the system} & & \text{chemical reaction} & & \text{system} \end{array}$$

or

$$\frac{dn_H}{dt} = \Gamma_H V - N_H \quad (5.10)$$

where;

n_H : moles of water in the control volume at any time

N_H : rate of water loss

From the definition of rate of reaction and the stoichiometry of the reaction (equation 5.3) it is possible to relate the rate of consumption of component A (o-p-HMP) to the rate of generation of component H (water)(4); $-2\Gamma_A = \Gamma_H$. Therefore, equation 5.10 can be written as:

$$\frac{dn_H}{dt} = -2\Gamma_A V - N_H \quad (5.11)$$

Replacing equation 5.9 in equation 5.11 and rearranging,

$$\frac{dn_H}{dt} = \frac{2n_{A0}(F - 1)}{V} \frac{dV}{dt} - 2n_{A0} \frac{dF}{dt} - N_H \quad (5.12)$$

As it was mentioned before the control volume corresponds to the volume occupied by the liquid resin, thus,

$$V = V_r + V_H \quad (5.13)$$

where V_r is the volume occupied by the resin solids and V_H is the volume occupied by the water. Equation 5.13 can be written as:

$$V = \frac{n_{A0} M_{A0}}{\rho_A} + \frac{n_H M_H}{\rho_H} \quad (5.14)$$

where;

- M_{A0} : molecular weight of the prepolymer (constant)
- ρ_A : density of the resin solids (constant)
- M_H : molecular weight of the water (constant)
- ρ_H : density of water (constant)

In the first term of equation 5.14 it is assumed that the volume of solids is constant and therefore independent of time. Replacing the volume in equation 5.12 and rearranging,

$$\frac{dn_H}{dt} = C_1 \frac{dF}{dt} - C_2 N_H \quad (5.15)$$

where;

$$C_1 = \frac{-2n_{A0}(n_h \rho_A M_H + n_{a0} \rho_H M_{A0})}{n_H \rho_A M_H + n_{A0}[\rho_H M_{A0} + 2\rho_A M_H (1 - F)]} \quad (5.16)$$

and

$$C_2 = \frac{n_h \rho_A M_H + n_{a0} \rho_H M_{A0}}{n_H \rho_A M_H + n_{A0}[\rho_H M_{A0} + 2\rho_A M_H (1 - F)]} \quad (5.17)$$

Energy Balance for the Liquid Resin

The energy balance is performed to obtain the rate of water loss due to evaporation. It is known that (4):

$$N_H = \frac{Q}{\lambda} \quad (5.18)$$

where Q is the total energy supplied to the control volume per unit time and λ is the latent heat of vaporization of water. The total energy Q can be written as:

$$Q = Q_1 + Q_2 \quad (5.19)$$

with Q_1 as the energy supplied by the surrounding environment and Q_2 as the energy supplied by the exothermic polymerization reaction. Thus, for Q_1 :

$$Q_1 = U (T_e - T_a) \quad (5.20)$$

where U is the global heat transfer coefficient, T_e is the temperature of the surrounding environment and T_a is the temperature of the adhesive (resin system). On the other hand, Q_2 can be written as:

$$Q_2 = \Delta H_r [-\Gamma_A V] \quad (5.21)$$

where ΔH_r is the heat of the reaction. This parameter is a function of the temperature of the environment, henceforth it will be defined as $\Delta H_r(T_e)$. Replacing equations 5.9 and 5.14 in equation 5.21 and rearranging:

$$Q_2 = \Delta H_r (T_e) \left[\frac{n_{a0} \rho_A M_H (F - 1)}{n_H \rho_A M_H + n_{a0} \rho_H M_{a0}} \frac{dn_h}{dt} - n_{a0} \frac{dF}{dt} \right] \quad (5.22)$$

Kinetics of the Polymerization Reaction

In Chapter 2 it was mentioned that the cure kinetics of thermosets can be described using a general n th order rate equation (equation 2.2). In addition, a simple Arrhenius expression can be chosen for describing the rate of heat evolved from the cure reaction (equation 2.3). Thus, a generalized expression for the fractional extent of conversion in terms of the order of the reaction (n), the Arrhenius frequency factor (A) and the activation energy of the reaction (E) can be obtained:

$$\ln \left[\frac{dF}{dt} \right] = \ln A - \frac{E}{RT_e} + n \ln [1 - F] \quad (2.6)$$

with R as the gas constant.

As it was explained in a previous chapter the introduction of water vapor at atmospheric pressure increases the gelation time of the resin system. This effect is suggesting that there is a slower rate of solvent water loss and thus a greater activation energy for polymerization. Therefore, the activation energy must be a function of the amount of water present in the resin and consequently, a function of the concentration of phenol-formaldehyde. Thus, equation 2.6 can be written as:

$$\ln \left[\frac{dF}{dt} \right] = \ln A - \frac{E(C_A)}{RT_{\theta}} + n \ln [1 - F] \quad (5.23)$$

Determination of the Activation Energy

To determine the relationship between activation energy and concentration of phenol-formaldehyde a general differential isoconversional method (5) must be used. The basic equation for the method is given by,

$$\ln \left[\frac{dF}{dt} \right]_i = \ln [f(F_i) A] - \frac{E}{RT_{\theta i}} \quad (5.24)$$

where the subscript, i, refers to the value of the variable at F_i degree of conversion and $f(F)$ corresponds to $(1-F)^n$. Two or more experiments must be performed at different environmental temperatures and different initial phenol-formaldehyde concentrations. For each experiment, values for temperature and dF/dt are obtained for various values of F_i (e.g. $F_i = 0.1, 0.3, \dots, 0.95$) covering the experimental range. Values for E/R and $\ln [f(F_i) A]$ at each value of F_i are obtained from the slope and intercept of equation 5.24. Parallel lines with a constant slope must be obtained. Thus, from a plot of activation energy versus phenol-formaldehyde initial concentration the best possible empirical relationship can be derived.

The activation energy as a function of concentration, $E(C_A)$, can be further developed to obtain its dependency as a function of the extent of conversion and the

amount of water at any given time:

$$E = f(C_A) = f\left[\frac{n_{A0}[1 - F]}{V}\right] \quad (5.25)$$

Replacing equation 5.14 in equation 5.25 and rearranging:

$$E = C_{A0} f\left[\frac{[1 - F]}{1 + C_3 n_H}\right] \quad (5.26)$$

where C_3 equals,

$$C_3 = \frac{\rho_A M_H}{\rho_H n_{A0} M_{A0}} \quad (5.27)$$

Using the Model

A set of equations has already been defined to model the curing process of aqueous phenol-formaldehyde under different water vapor environments. It is necessary to have experimental data for the extent of conversion and for the temperature of the adhesive as a function of time at different environmental temperatures. From these data the best possible curve fit equations must be obtained. Thus, empirical relationships for

F, dF/dt and T_a as a function of time at a given environmental temperature will be available. In addition, it is necessary to have experimental data for the heat of the reaction at different temperatures to be used in solving the energy balance. Replacing the correspondent empirical relationships for these parameters in equations 5.15, 5.20 and 5.22, a single differential equation for the amount of water as a function of time at a given environmental temperature must be obtained. At different water vapor and temperature conditions different coefficients will fit the empirical relationships and different rates of water loss must be expected. A numerical solution of the differential equation must be performed. The Runge-Kutta algorithm could be a good method to solve this equation (6, 7). The next step in the model would be to solve equation 5.23 to determine the kinetic parameters. As it was mentioned previously, before solving the kinetic equation an empirical relationship for the activation energy as a function of concentration of the resin must be obtained. Thus, the effect of water vapor pressure will be reflected in the kinetic equation through the dependency of the activation energy with the amount of water remaining in the system at a given time.

Equation 5.23 is a function of time with only two unknown parameters (order of the reaction and frequency factor). Therefore, it can be written as,

$$\ln \left[\frac{dF}{dt} + \frac{E(F, n_H)}{RT_\theta} \right] = \ln A + n \ln (1 - F) \quad (5.28)$$

providing a form suitable for regression analysis (8):

$$Z = a + bX \tag{5.29}$$

where $a = \ln A$, and $b = n$. Thus, from the intercept and slope of equation 5.29 the kinetics parameters can be determined.

An easy way to visualize the procedure proposed here to obtain the kinetics parameters of the polymerization reaction, is presented in table 5.1;

Table 5.1 Illustrative table of results for a given water vapor pressure

T	time	n_H	F	dF/dt	A	n
T_1	t_1	n_{H1}	F_1	$(dF/dt)_1$	A_1	n_1
	t_2	n_{H2}	F_2	$(dF/dt)_2$		
	t_3	n_{H3}	F_3	$(dF/dt)_3$		
T_2	t_1	n_{H1}	F_1	$(dF/dt)_1$	A_2	n_2
	t_2	n_{H2}	F_2	$(dF/dt)_2$		
	t_3	n_{H3}	F_3	$(dF/dt)_3$		
T_3	t_1	n_{H1}	F_1	$(dF/dt)_1$	A_3	n_3
	t_2	n_{H2}	F_2	$(dF/dt)_2$		
	t_3	n_{H3}	F_3	$(dF/dt)_3$		

For each temperature at a given water vapor pressure the kinetic equation must be solved and, therefore, a value for A and n must be obtained for each set of temperature

conditions. Once the order of the reaction and the frequency factor have been obtained for each combination of environmental temperature and water vapor pressure, a possible dependence of these parameters with these variables can be determined. Thus, the effect of environmental temperature and water vapor pressure on the rate of the reaction can be modelled.

Expected Effect of Water Vapor Pressure on the Kinetics Parameters

The frequency factor A is a function of the collisions probability of the reactants (9, 10) and, thus, related to the mobility of the species. It is known that the introduction of water vapor at atmospheric pressure increases the gelation time of the resin suggesting a slower rate of water loss. The polymerization of phenol-formaldehyde is a condensation reaction with water as a product. This means that water vapor will participate in the equilibrium of each of the many possible condensation steps and it will be affecting the concentration of the phenol-formaldehyde with time. Then, it is reasonable to expect that $\ln A$ will increase with an increase in water vapor pressure due to an increase in the mobility of the polymer molecules as a consequence of a more diluted system.

The order of the reaction refers to the powers to which the concentrations of the individual reacting species are raised in the kinetic rate law. The overall order of the reaction, n , is given by the summation of every individual power. As it was mentioned above the presence of water vapor will affect the position of condensation equilibria and thus the rate of any condensation reaction. Moreover, the polymerization of phenol-

formaldehyde is a complex multipath reaction system which involves simultaneous and sequential reaction steps. If elevated water vapor pressures can alter the rate of one or more condensation pathways, then alternative reaction pathways will be more or less able to compete for reactants. In other words, changing the rate of one reaction pathway could enhance or inhibit other reaction steps. Therefore, it could be expected to have a relative preponderance of one or more specific coupling reactions depending upon the moisture conditions during cure. On the other hand, Lindemann (11) developed a theory based on interaction or collision between molecules whereby the concentration of the reacting species can alter the order of a nonelementary reaction. Thus, the reaction orders for the polymerization of phenol-formaldehyde under different water vapor environments should be different.

Summary

A mathematical model of the cure kinetics of phenol-formaldehyde has been presented. The model is based on the occurrence of two simultaneous reactions; condensation polymerization and evaporation. The effect of environmental temperature is taken into account through an Arrhenius expression for the constant of the reaction in the kinetic equation and, in an energy balance needed for the determination of the amount of water present in the system at any time. The effect of water vapor pressure is considered in the kinetic equation through the dependency of the activation energy for polymerization with the concentration of the resin at any time. The application of the

model should shed light on the influence of water vapor environments on the kinetic parameters A and n. The model could not be tested because it was not possible to determine the variation of extent of conversion with time from the information given by the techniques used to characterize the polymerization reaction.

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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The intent of this research was to enhance our knowledge of aqueous phenol-formaldehyde resin cure as it is affected by the elevated water vapor pressures that occur during hot-pressing of a wood-based composite. The cure reaction was monitored at different temperatures and water vapor pressures. The time to gelation was used as the variable to monitor the cure reaction and, the glass transition temperature and the degree of cross-linking were used to characterize the resulting resin-network.

The polymerization reaction of aqueous phenol-formaldehyde thermosetting adhesive above atmospheric pressure was characterized using microdielectric spectroscopy and gel time measurements. The time to gelation as measured by the gel time technique correlate fairly well with times as measured by microdielectric spectroscopy even though each of these methods probe different material properties. As the temperature of the experiment increases, the time to gelation decreases, and an increase in the water vapor pressure (below saturated conditions) of the system results in an increase in the time to gelation.

Thermomechanical analysis and swelling tests showed to be effective techniques for studying the glass transition temperature, the cross-link density, and the molecular weight between cross-links of a cured phenol-formaldehyde resin network. During the

curing process under elevated water vapor pressure some water is trapped into the resin network and acts as a plasticizer. The presence of water affects the cross-link density and the glass transition temperature of such a network. As the water vapor pressure during polymerization increases the glass transition temperature and the cross-link density of the cured resin-network decreases. In addition, scanning electron microscopy showed that water vapor environments may alter the morphology of the cured phenol-formaldehyde.

A theoretical approach to model the cure kinetics of phenol-formaldehyde has been developed. The model is based on the occurrence of two simultaneous reactions (condensation polymerization and evaporation of water) and on the concentration dependency of the activation energy of polymerization. The application of the model should shed light on how time, temperature and water vapor pressure are affecting the kinetics parameters A (Arrhenius frequency factor) and n (order of the reaction).

Recommendations

Further work is needed to better understand the cure behavior of phenolic resins under different water vapor conditions. An understanding of the influence of elevated water vapor pressure during cure on the morphology, molecular structure, and molecular dynamics of the cured resin is essential.

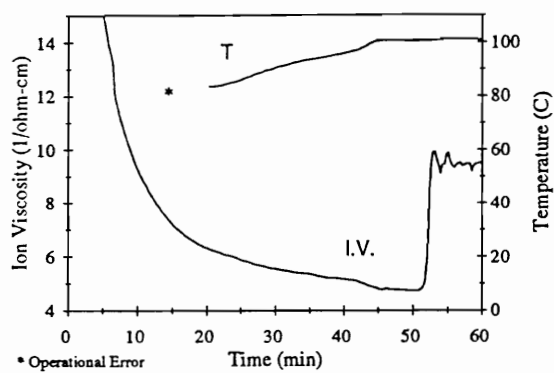
Microdielectric spectroscopy and gel time measurements are not suitable techniques to monitor the early stages of polymerization for this adhesive system. Fourier transform infrared spectroscopy (FT-IR) has been reported to be a successful technique to monitor the cure reaction of thermosetting systems. Thus, FT-IR could be an

alternative technique for characterizing chemical changes during the process of cure of aqueous phenol-formaldehyde. From the information given by this technique, the variation of the extent of the conversion with time can be calculated and the theoretical model developed in this research can be tested. Thus, the kinetic parameters of the curing reaction of aqueous phenol-formaldehyde can be determined.

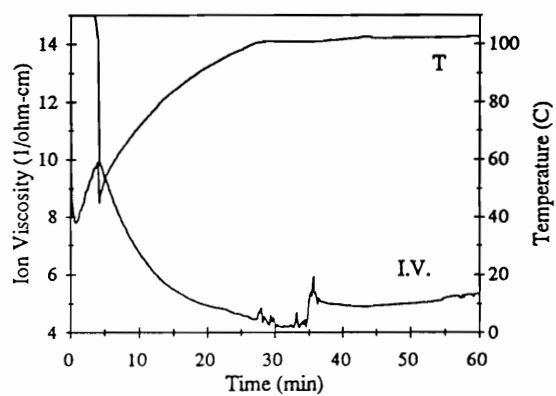
Up to this point, consideration has only been given to the complexities inherent during the interplay of alkaline phenol, formaldehyde, and water. The situation could be much different in the presence of wood. It might be expected that the wood substrate will alter the cure kinetics and the properties of the adhesive system. Indeed, evidence of this effect has been reported in the literature where mention has been made of wood's ability to preferentially absorb low molecular weight methylolphenols. This could alter the rate of resin cure and reduce the plasticity of the adhesive. Therefore, a future area of research should be the study of the curing process of phenol-formaldehyde under elevated water vapor pressures in the presence of wood.

APPENDIX A: DEA Spectra

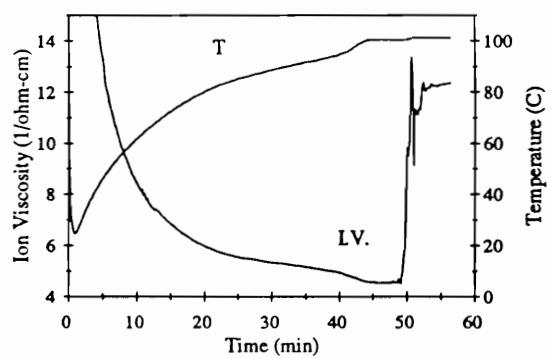
APPENDIX A: DEA Spectra



(a)

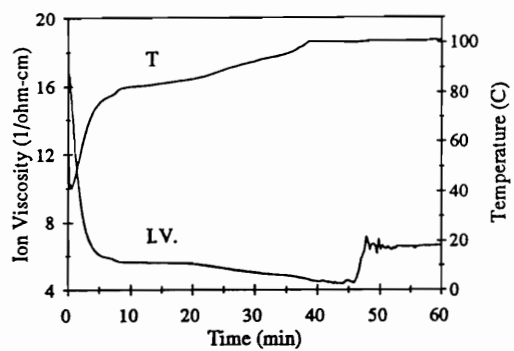


(b)

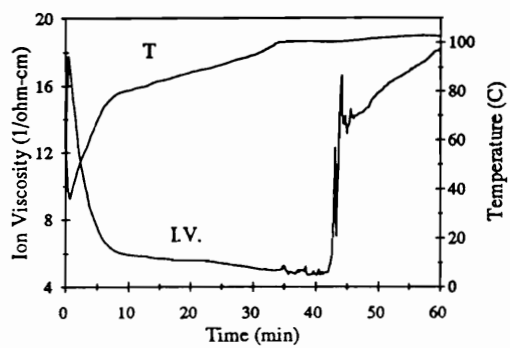


(c)

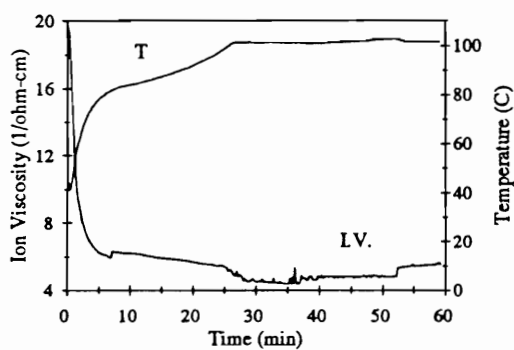
Figure A1 $P < 7 \text{ kPa}$; $T = 100 \text{ C}$, runs (a), (b) and (c)



(a)

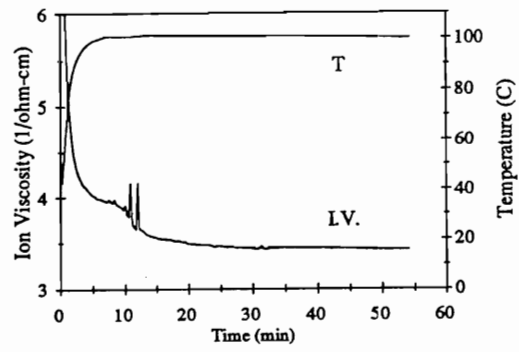


(b)

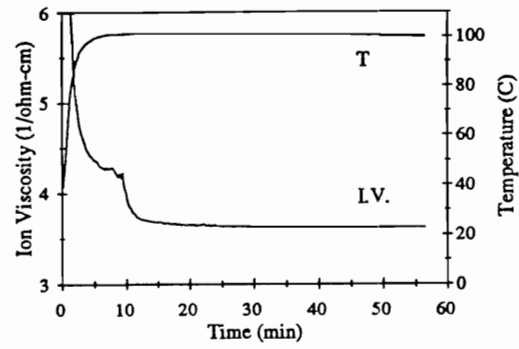


(c)

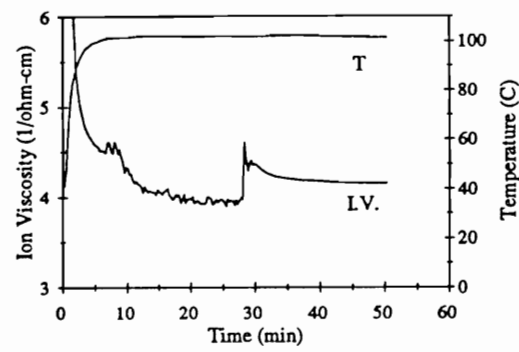
Figure A2 $P = 97 \text{ kPa}$; $T = 100 \text{ C}$, runs (a), (b) and (c)



(a)

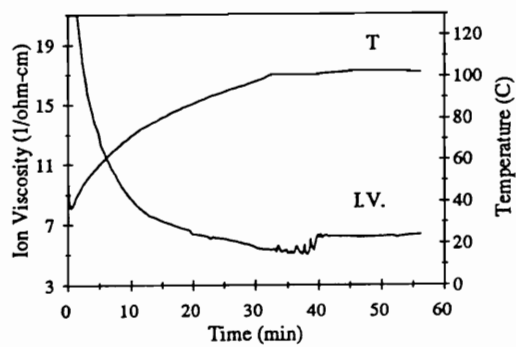


(b)

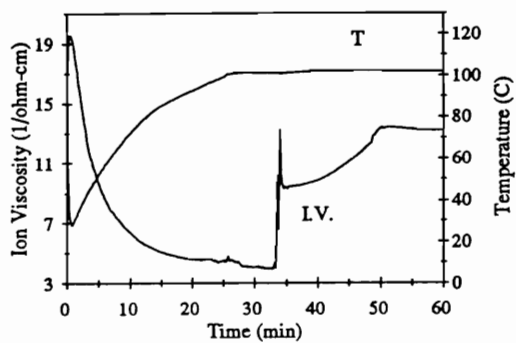


(c)

Figure A3 $P = 97 \text{ kPa}$, sat; $T = 100 \text{ C}$, runs (a), (b) and (c)

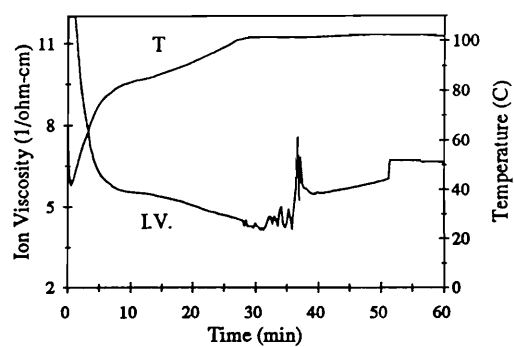


(a)

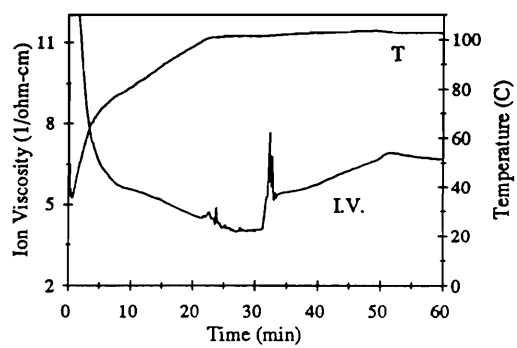


(b)

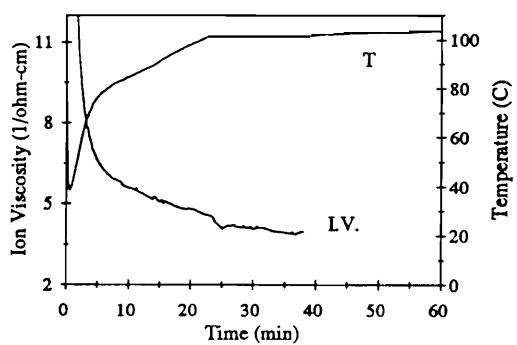
Figure A4 $P < 7$ kPa, $T = 110$ C, runs (a) and (b)



(a)

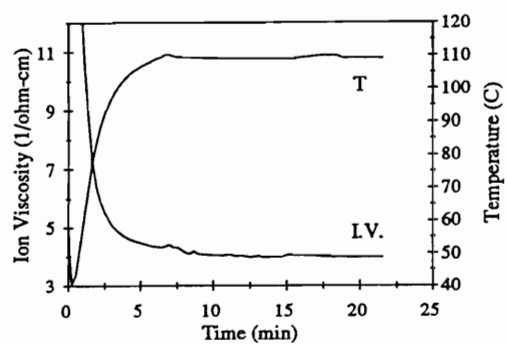


(b)

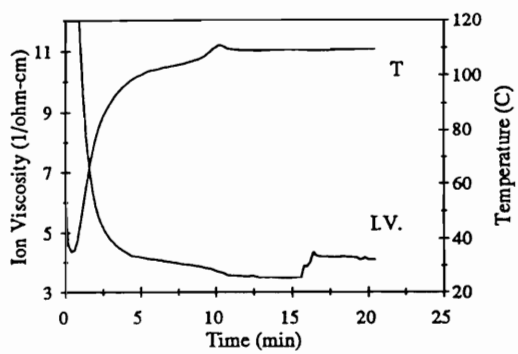


(c)

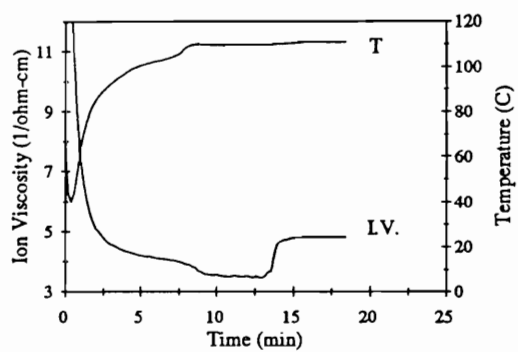
Figure A5 $P = 97 \text{ kPa}$, $T = 110 \text{ C}$, runs (a), (b) and (c)



(a)

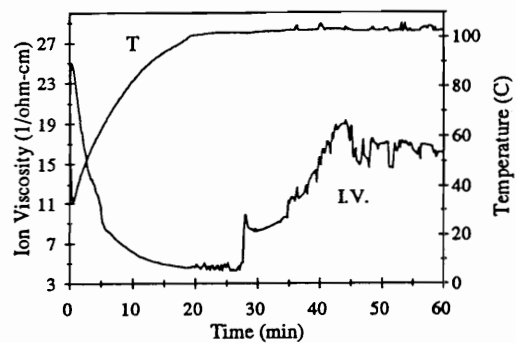


(b)

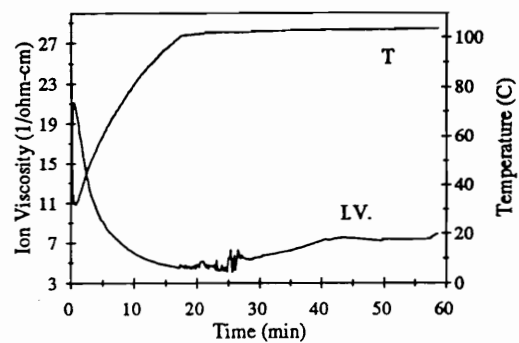


(c)

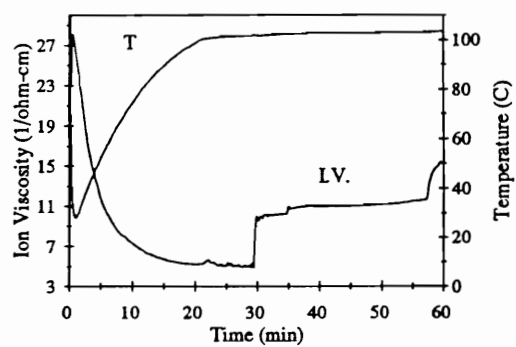
Figure A6 $P = 138 \text{ kPa}$; $T = 110 \text{ C}$, runs (a), (b) and (c)



(a)

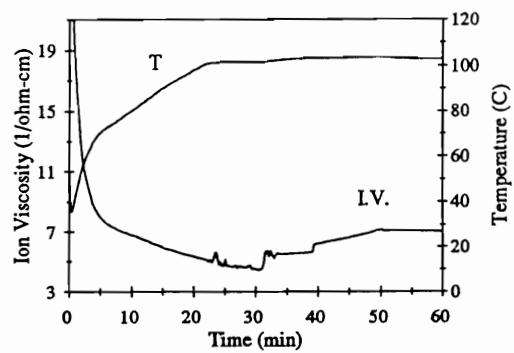


(b)

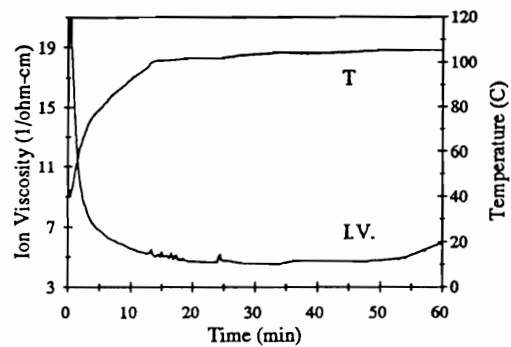


(c)

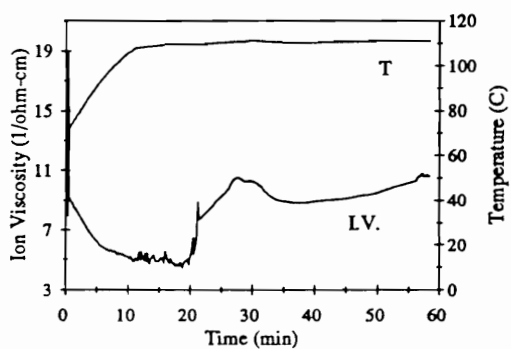
Figure A7 $P < 7 \text{ kPa}$; $T = 120 \text{ C}$, runs (a), (b) and (c)



(a)

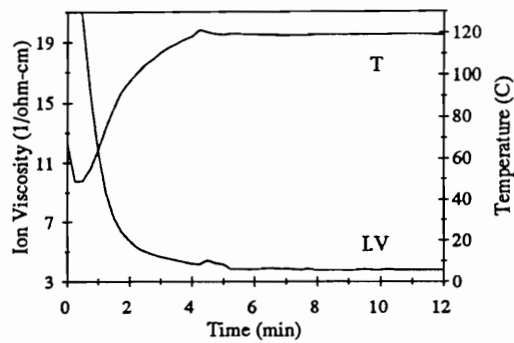


(b)

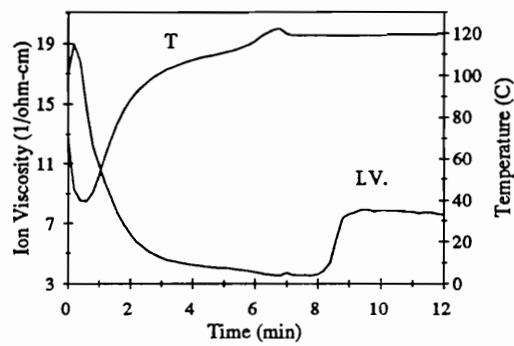


(c)

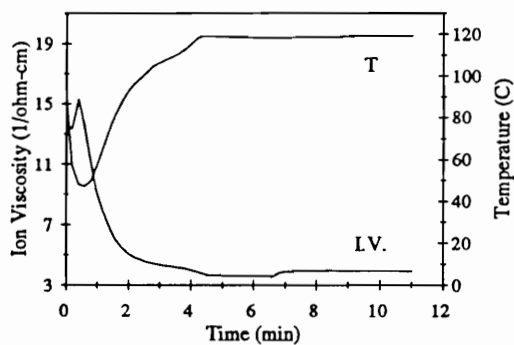
Figure A8 $P = 97 \text{ kPa}$; $T = 120 \text{ C}$, runs (a), (b) and (c)



(a)

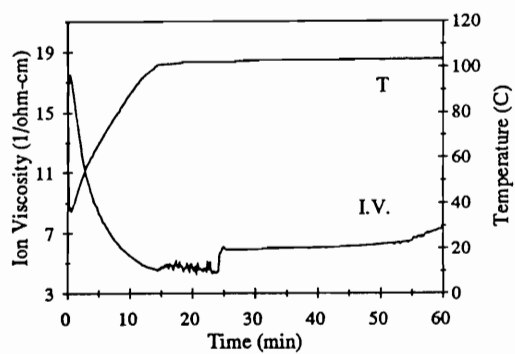


(b)

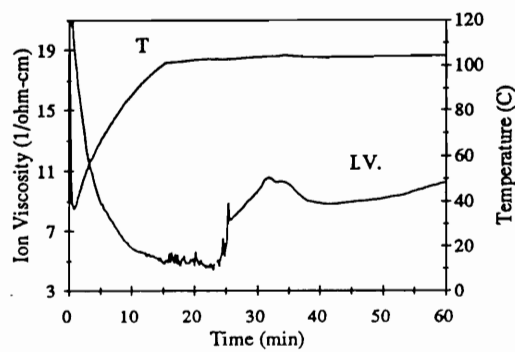


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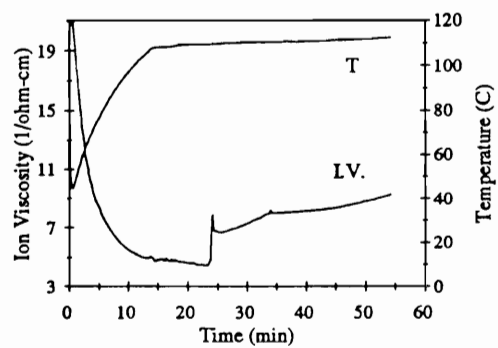
Figure A9 $P = 200 \text{ kPa}$; $T = 120 \text{ C}$, runs (a), (b) and (c)



(a)

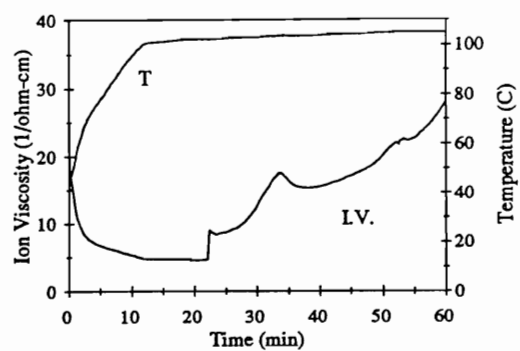


(b)

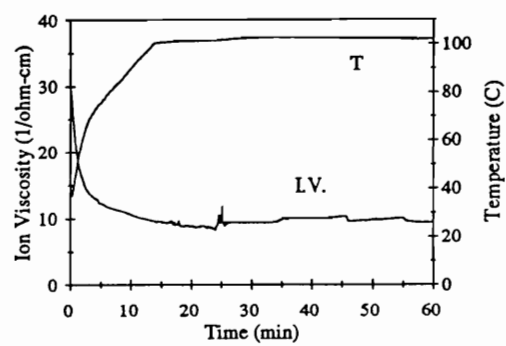


(c)

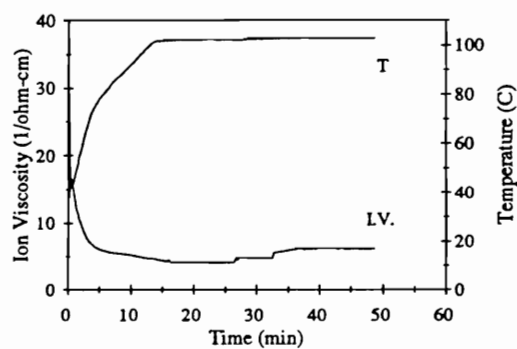
Figure A10 $P < 7 \text{ kPa}$; $T = 130 \text{ C}$, runs (a), (b) and (c)



(a)

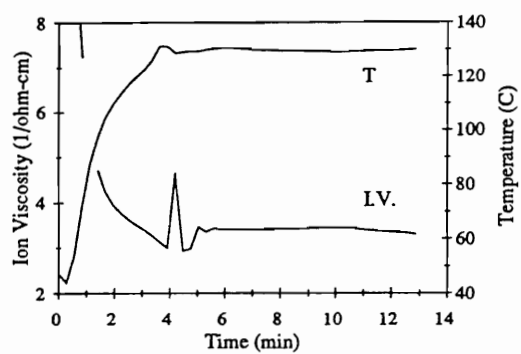


(b)

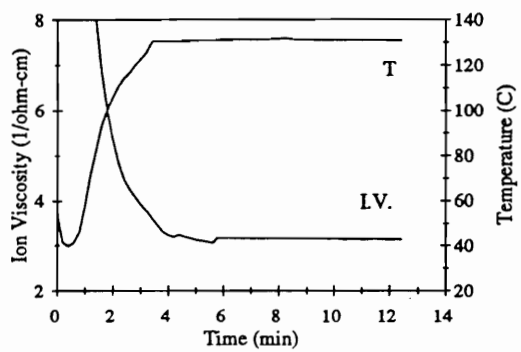


(c)

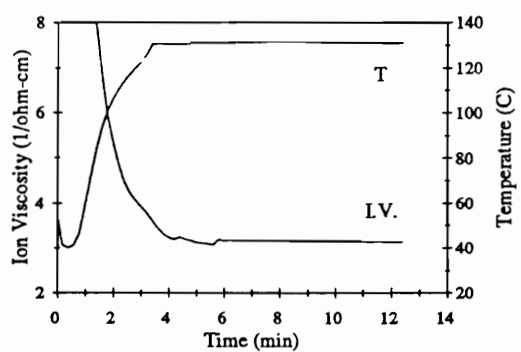
Figure A11 $P = 97 \text{ kPa}$; $T = 130 \text{ C}$, runs (a), (b) and (c)



(a)

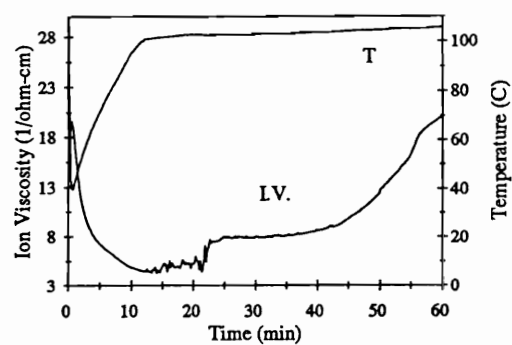


(b)

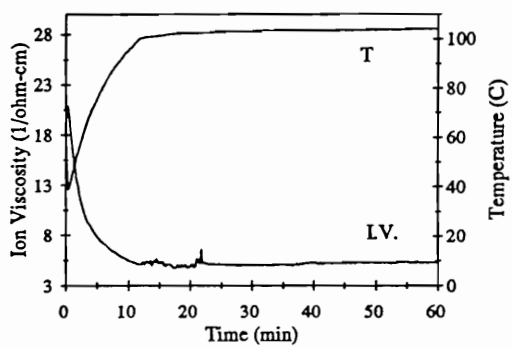


(c)

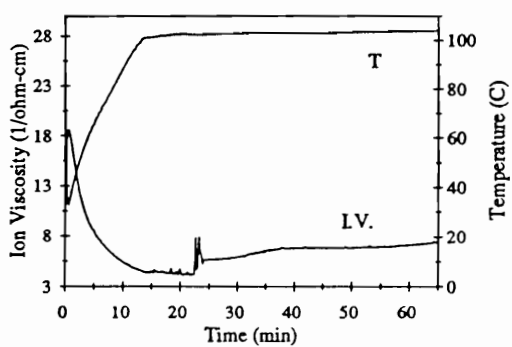
Figure A12 $P = 269 \text{ kPa}$; $T = 130 \text{ C}$, runs (a), (b) and (c)



(a)

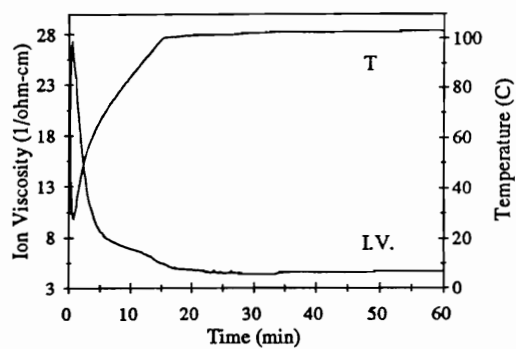


(b)

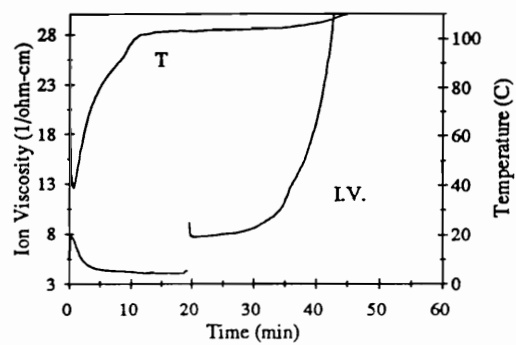


(c)

Figure A13 $P < 7 \text{ kPa}$; $T = 140 \text{ C}$, runs (a), (b) and (c)

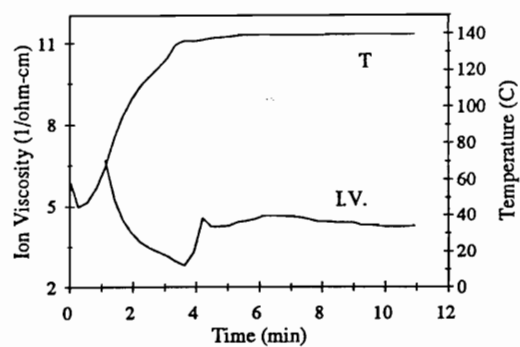


(a)

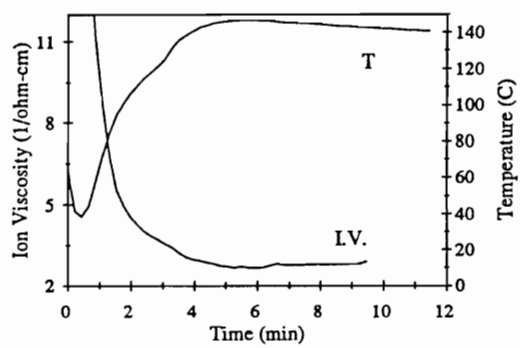


(b)

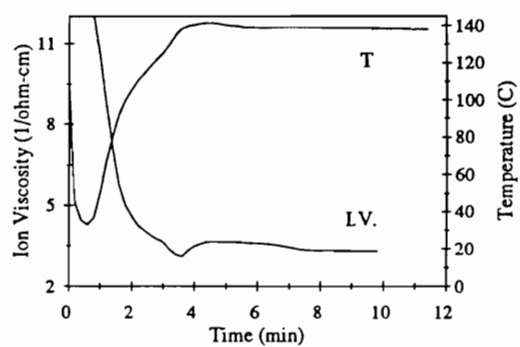
Figure A14 $P = 97 \text{ kPa}$; $T = 140 \text{ C}$, runs (a) and (b)



(a)



(b)

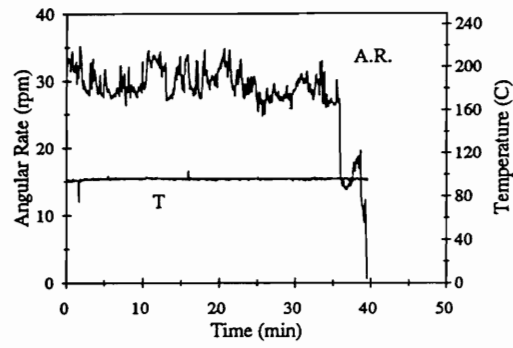


(c)

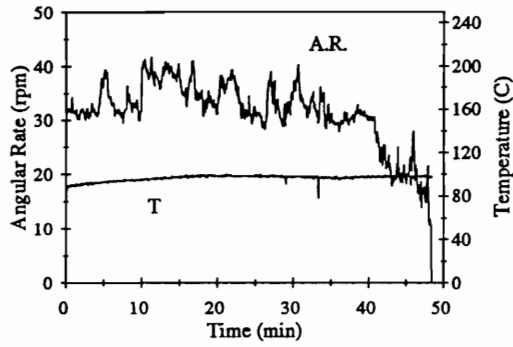
Figure A15 $P = 352 \text{ kPa}$; $T = 140 \text{ C}$, runs (a), (b) and (c)

APPENDIX B:

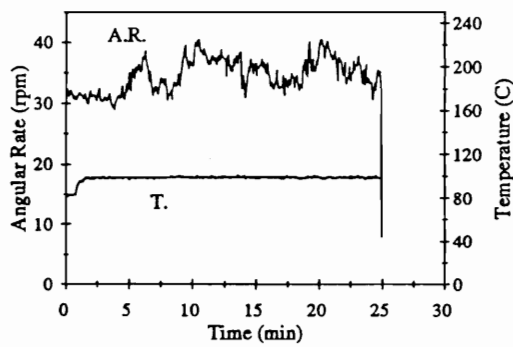
Gel Time Technique Spectra



(a)

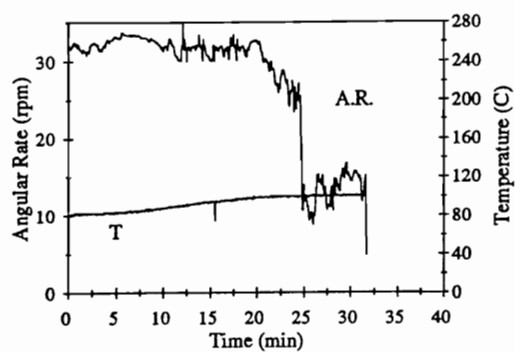


(b)

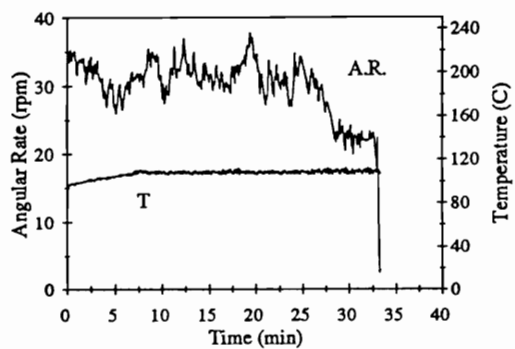


(c)

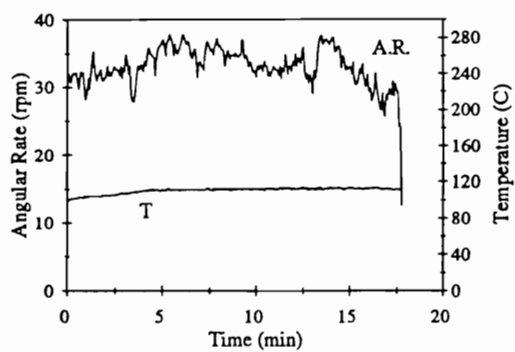
Figure B1 Runs at 100 C. (a) $P < 7$ kPa ; (b) $P = 97$ kPa ;
(c) $P = 97$ kPa, sat



(a)

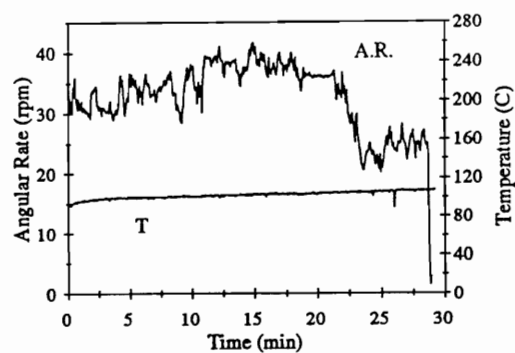


(b)

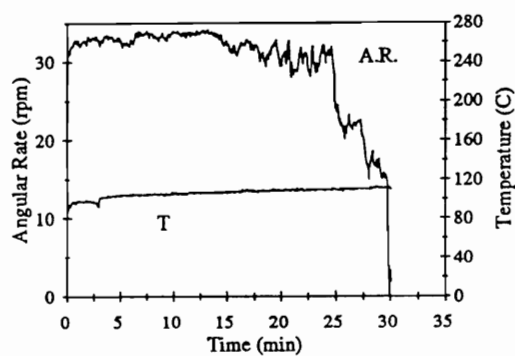


(c)

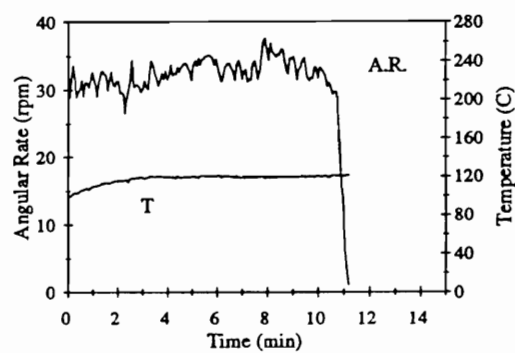
Figure B2 Runs at 110 C. (a) $P < 7 \text{ kPa}$; (b) $P = 97 \text{ kPa}$;
(c) $P = 138 \text{ kPa}$



(a)

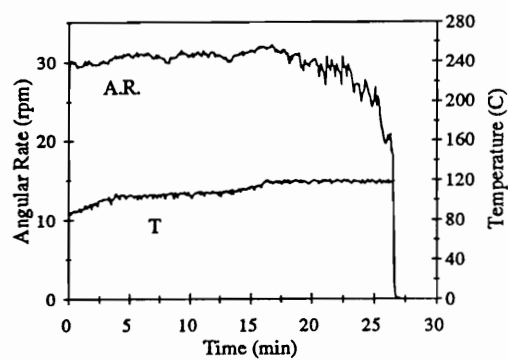


(b)

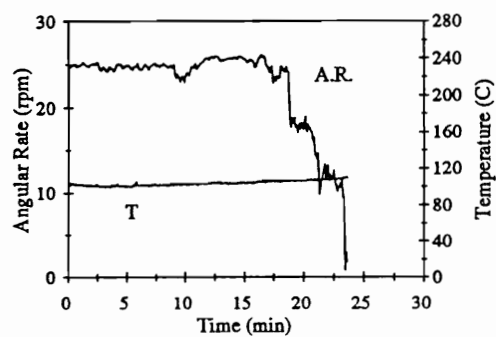


(c)

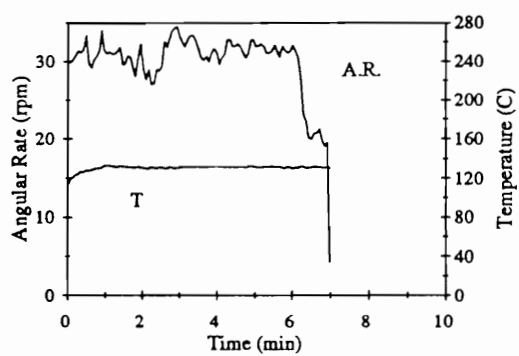
Figure B3 Runs at 120 C. (a) $P < 7$ kPa ; (b) $P = 97$ kPa ;
(c) $P = 200$ kPa



(a)

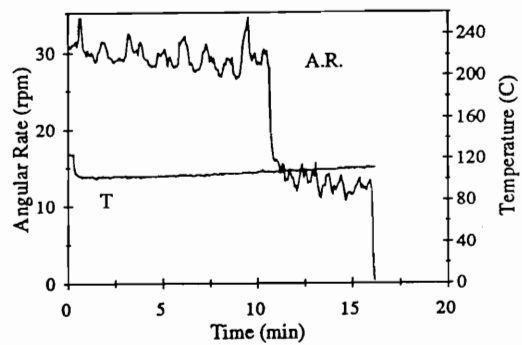


(b)

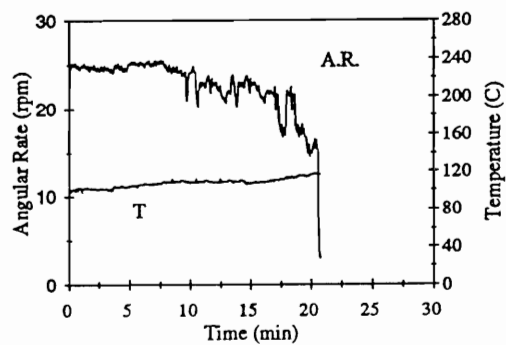


(c)

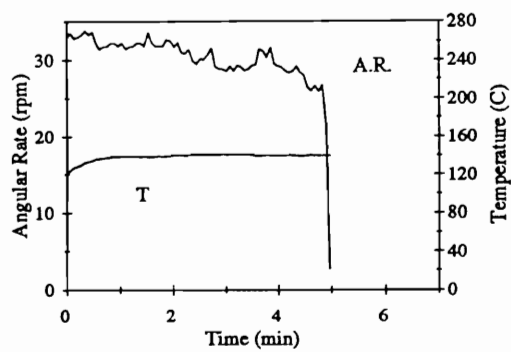
Figure B4 Runs at 130 C. (a) $P < 7 \text{ kPa}$; (b) $P = 97 \text{ kPa}$;
(c) $P = 269 \text{ kPa}$



(a)



(b)



(c)

Figure B5 Runs at 140 C. (a) $P < 7$ kPa ; (b) $P = 97$ kPa ;
(c) $P = 352$ kPa

APPENDIX C:

DSC Temperature Scan

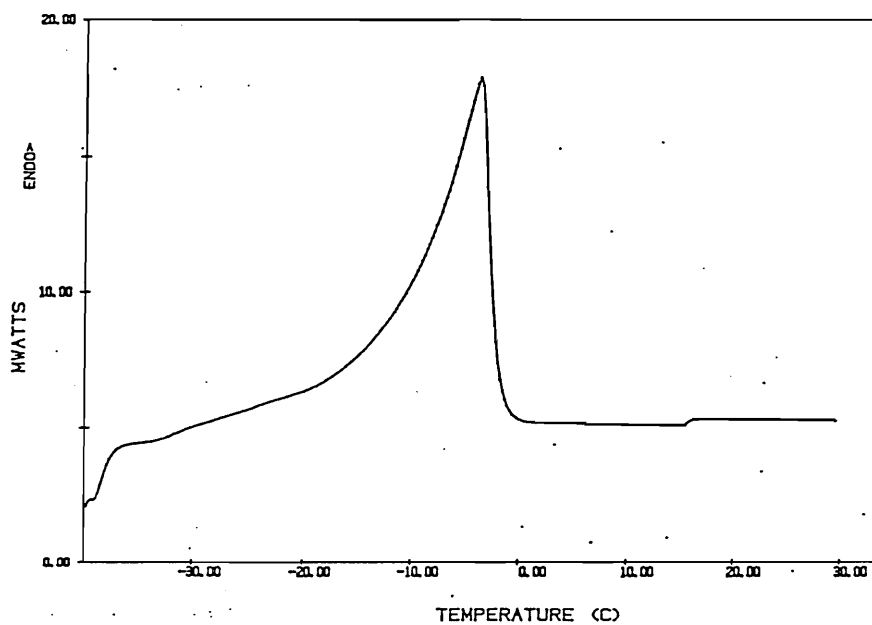
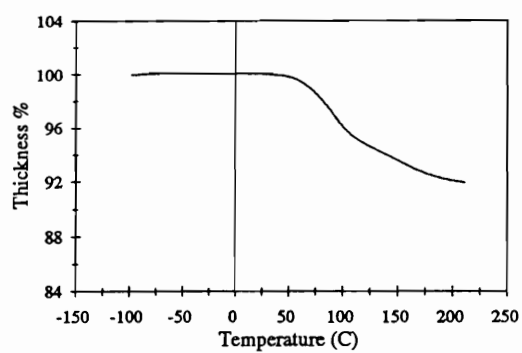
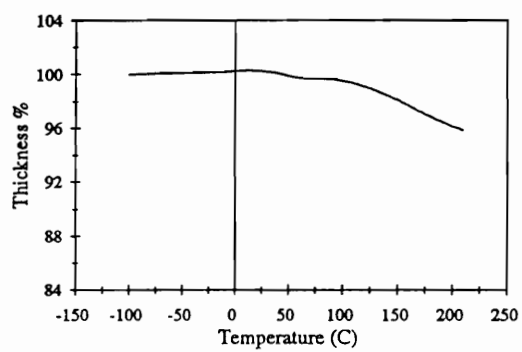


Figure C1 DSC temperature scan of the uncured phenolic resin

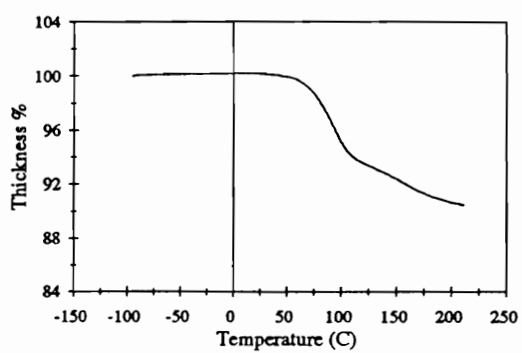
APPENDIX D: TMA Spectra



(a)

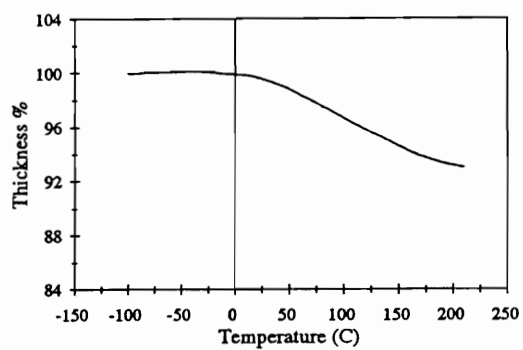


(b)

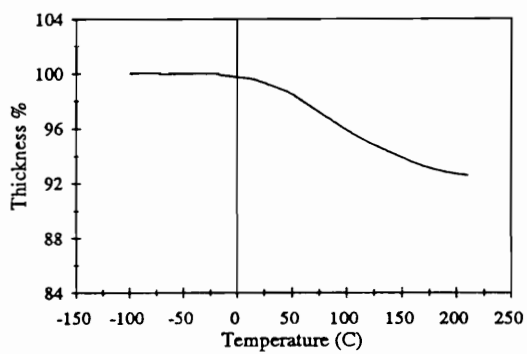


(c)

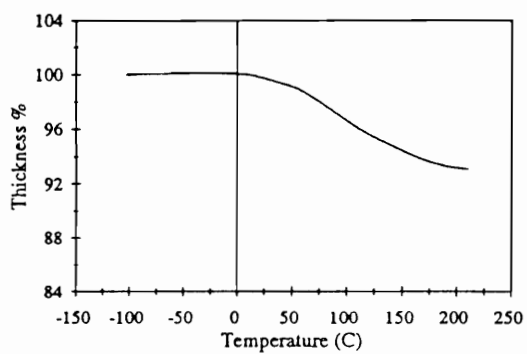
Figure D1 $P < 7 \text{ kPa}$; $T = 100 \text{ C}$, runs (a), (b) and (c)



(a)

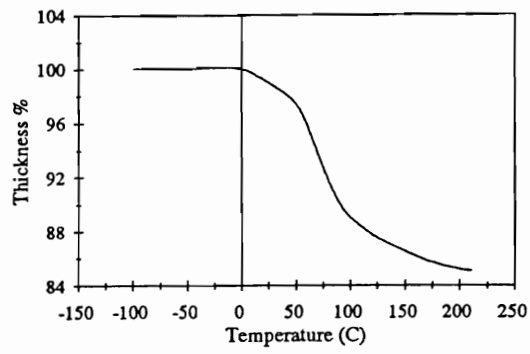


(b)

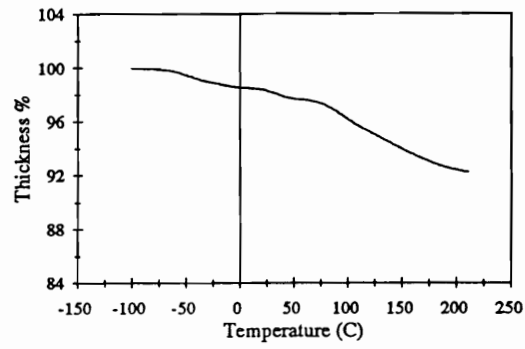


(c)

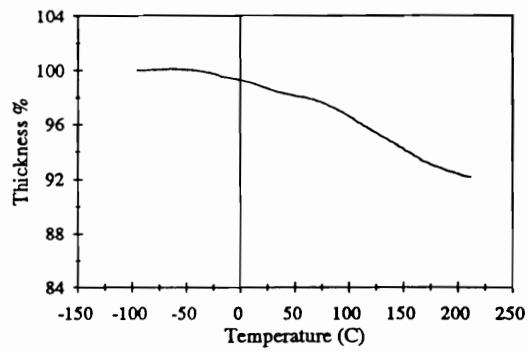
Figure D2 $P = 97 \text{ kPa}$; $T = 100 \text{ C}$, runs (a), (b) and (c)



(a)

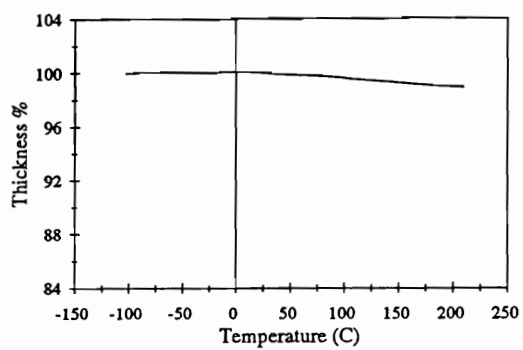


(b)

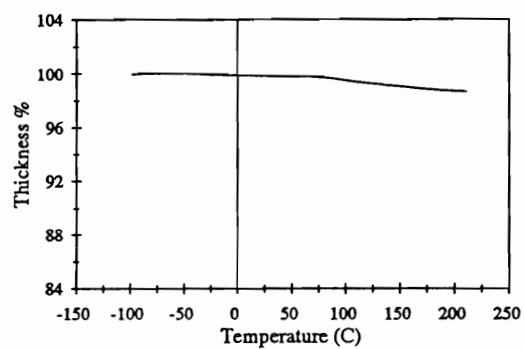


(c)

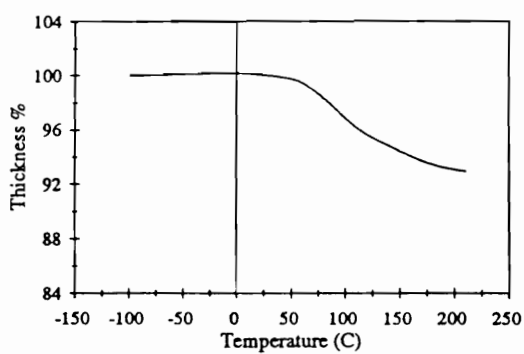
Figure D3 P = 97 kPa, sat.; runs (a), (b) and (c)



(a)

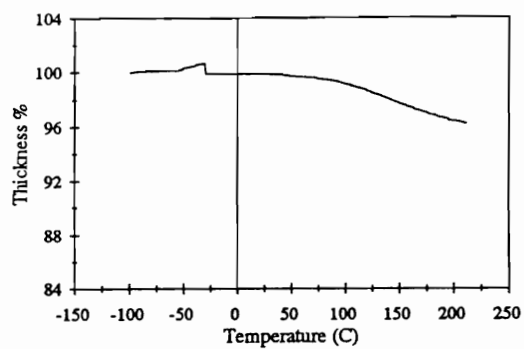


(b)

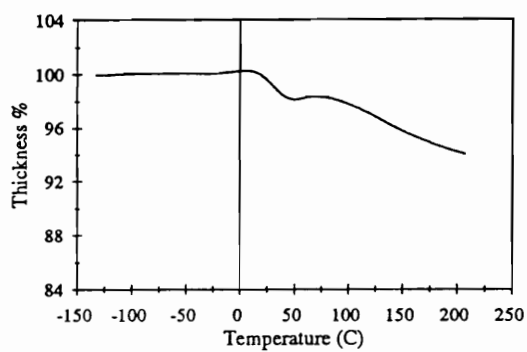


(c)

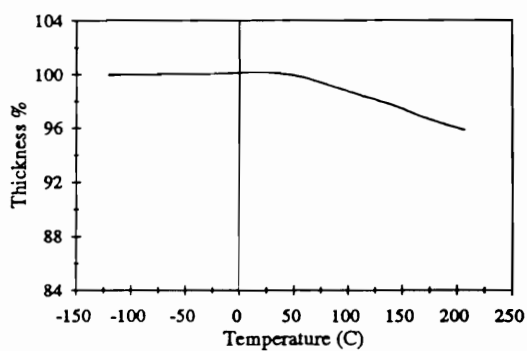
Figure D4 $P < 7 \text{ kPa}$; $T = 110 \text{ C}$, runs (a), (b) and (c)



(a)

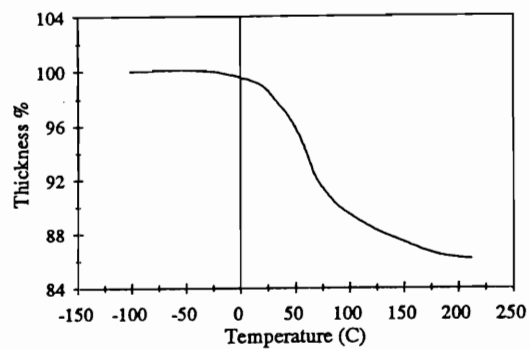


(b)

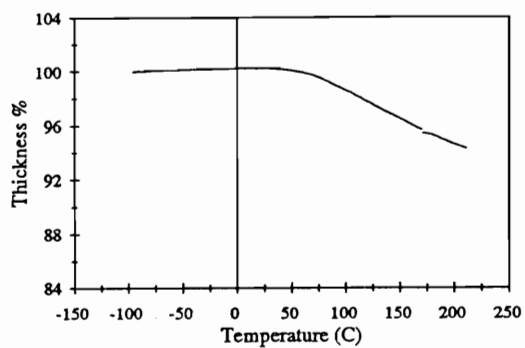


(c)

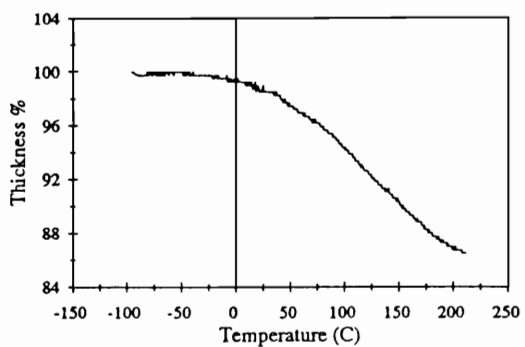
Figure D5 $P = 97 \text{ kPa}$; $T = 110 \text{ C}$, runs (a), (b) and (c)



(a)

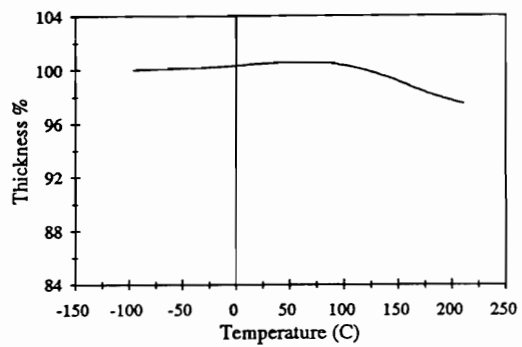


(b)

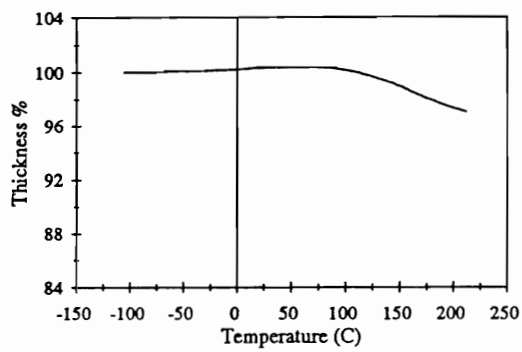


(c)

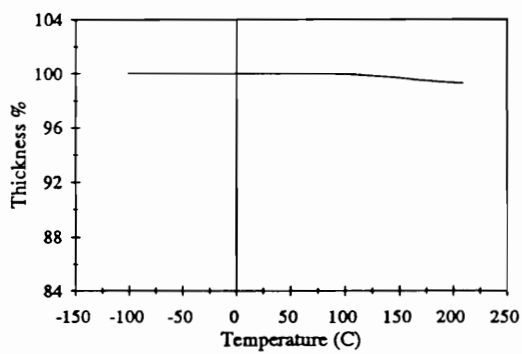
Figure D6 P = 138 kPa ; T = 110 C, runs (a), (b) and (c)



(a)

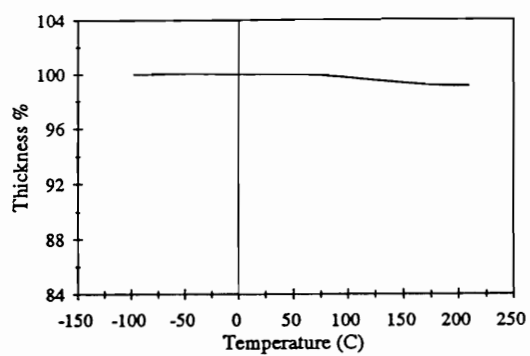


(b)

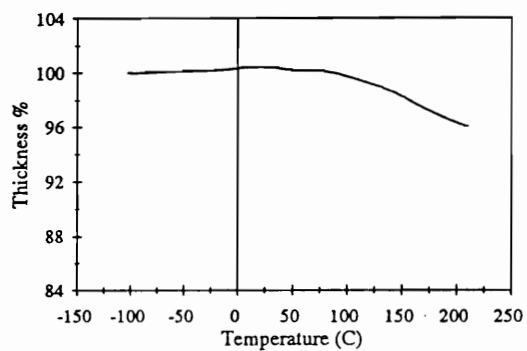


(c)

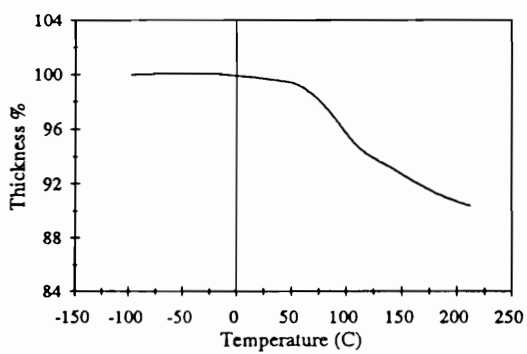
Figure D7 $P < 7 \text{ kPa}$; $T = 130 \text{ C}$, runs (a), (b) and (c)



(a)

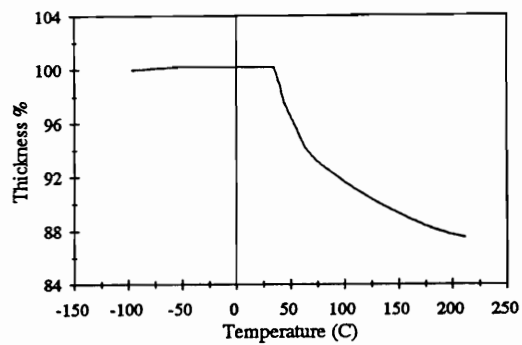


(b)

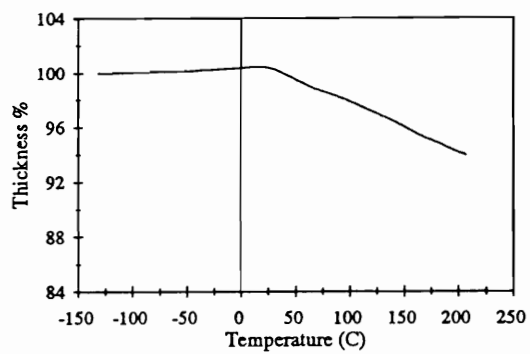


(c)

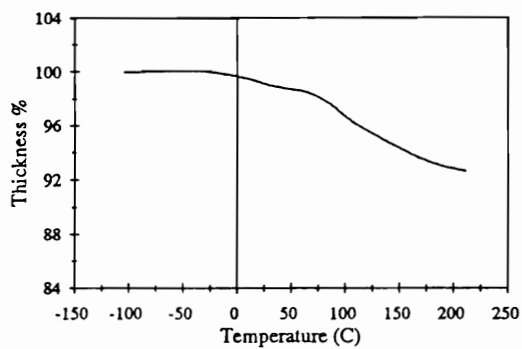
Figure D8 $P = 97 \text{ kPa}$; $T = 120 \text{ C}$, runs (a), (b) and (c)



(a)

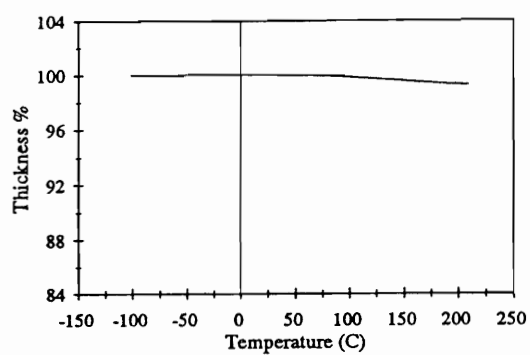


(b)

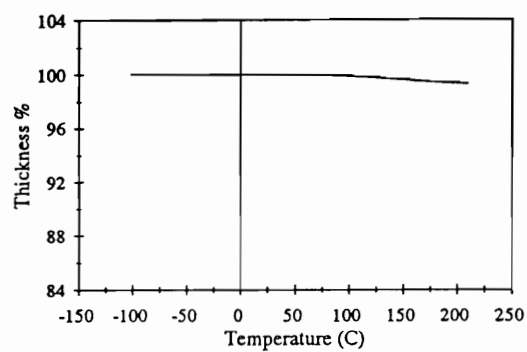


(c)

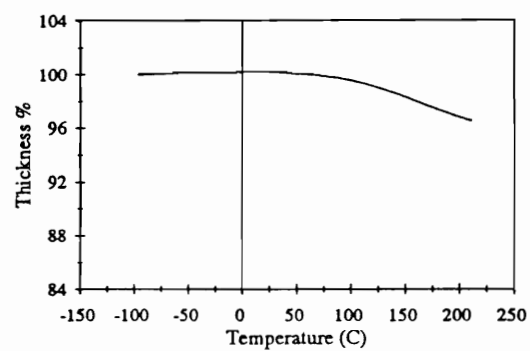
Figure D9 $P = 200 \text{ kPa}$; $T = 120 \text{ C}$, runs (a), (b) and (c)



(a)

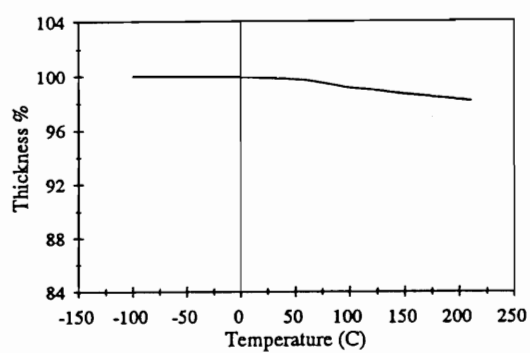


(b)

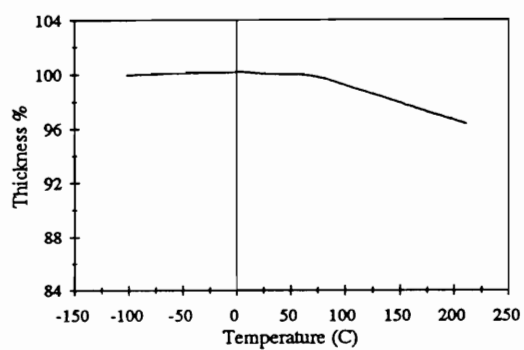


(c)

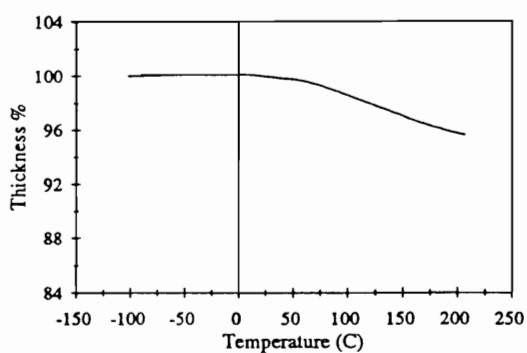
Figure D10 $P < 7$ kPa ; $T = 130$ C, runs (a), (b) and (c)



(a)

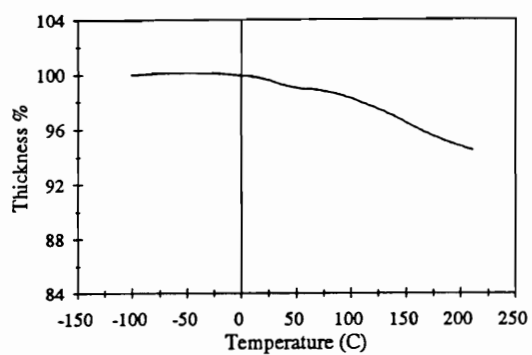


(b)

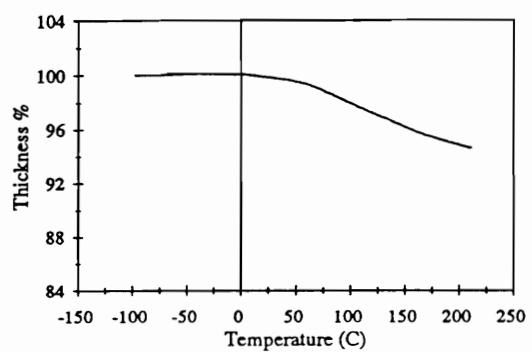


(c)

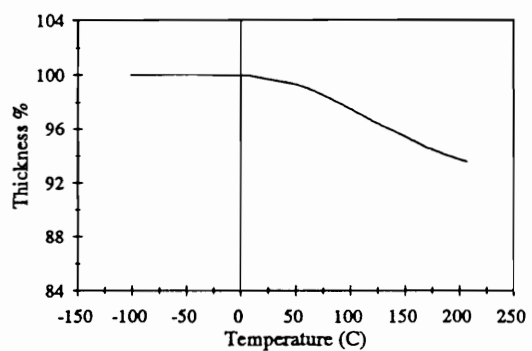
Figure D11 P = 97 kPa ; T = 130 C, runs (a), (b) and (c)



(a)

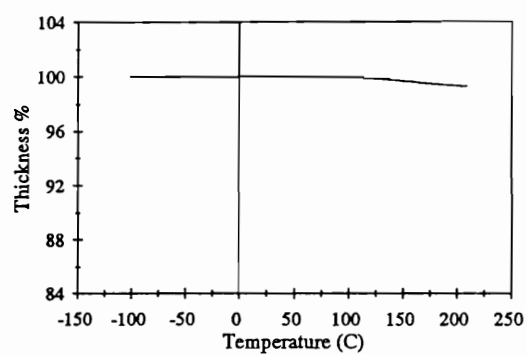


(b)

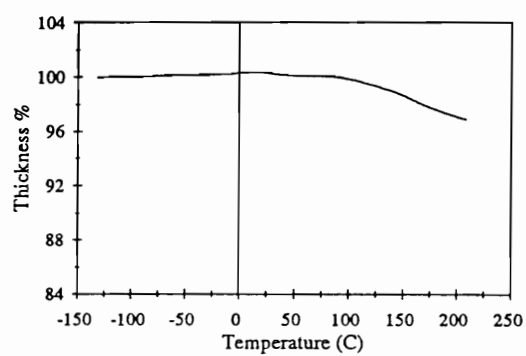


(c)

Figure D12 P = 269 kPa ; T = 130 C, runs (a), (b) and (c)

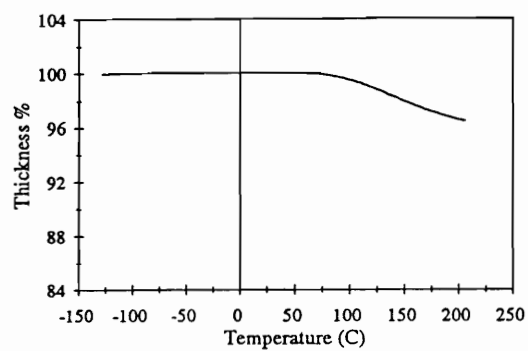


(a)

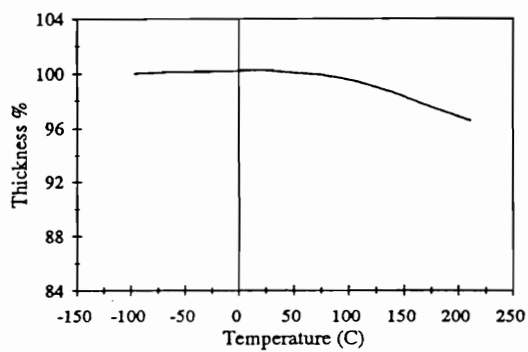


(b)

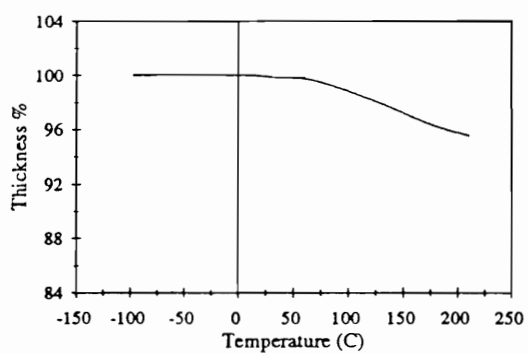
Figure D13 $P < 7 \text{ kPa}$; $T = 140 \text{ C}$, runs (a) and (b)



(a)

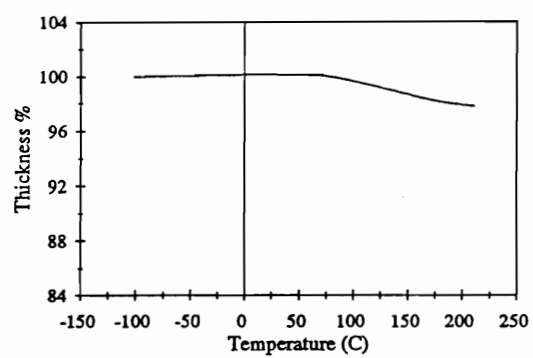


(b)

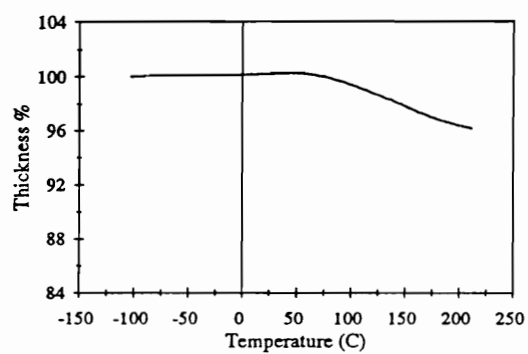


(c)

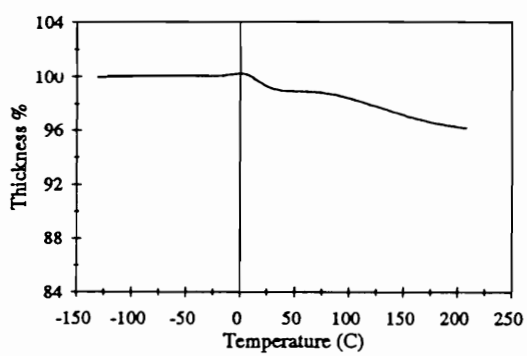
Figure D14 $P = 97 \text{ kPa}$; $T = 140 \text{ C}$, runs (a), (b) and (c)



(a)



(b)



(c)

Figure D15 P = 352 kPa ; T = 140 C, runs (a), (b) and (c)

VITA

The author was born in Concepción, Chile on February 9, 1961. He graduated from Liceo Enrique Molina Garmendia High School (Concepción) in December 1977.

In October 1985 he received his Bachelor of Science degree in Chemical Engineering with a specialization in Pulp and Paper from Universidad de Concepción (Chile). In October 1988 he received his Master of Science degree in Chemical Engineering from the same university. He enrolled at Virginia Polytechnic Institute and State University in September 1991 and began working toward a Doctor of Philosophy in Wood Science and Forest Products, which he completed in December 1994.

