LCMR FINAL STATUS REPORT - Detailed for Peer Review - Research

I.   **Means for Producing Lignin-Based Plastics; 9/18/91 - 9/30/93**

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A.   M.L. 91, Ch. 254, Art. 1, Sec. 14, Subd. 13 (f) Appropriation: $100,000
                                                        Balance: $ 0

Means for Producing Lignin-Based Plastics: This appropriation is to the commissioner of administration for a grant to the University of Minnesota, Department of Forest Products, to develop means for fabricating engineering plastics based upon industrial by-product lignins and corresponding raw materials from wheat straw.

B.   Compatible Data: not applicable

C.   Status of Match: not applicable

II.   **Narrative**

During pulp manufacture, cellulosic fibers for making paper are produced by removing lignins from wood chips. It has been forecast that in 1991 neither pulp mill at Cloquet nor International Falls, Minnesota, will be able to consume all of the byproduct lignins in the customary manner as fuel for the recovery furnace stage of the pulping operation. Consequently this project is devoted to devising methods applicable on an industrial scale for converting such excess aspen and Jack pine kraft lignins into preparations that can be used to fabricate biodegradable plastics. Corresponding materials will be fashioned through similar manipulations of Organosolv lignins from wheat straw as an agricultural residue. Hereby simple means will be sought for securing lignin derivative fractions composed only of those molecular components that can interact with one another to form extended well-defined arrangements in the solid state.

III. **Objectives**

A.   **Fractionation of lignin derivatives by methods amenable to scale-up**

A.1. *Narrative.* Lignin derivative fractions will be prepared through combinations of precipitation and ultrafiltration techniques.

A.2. *Procedures.* Lignin derivative fractions will be isolated by acidifying aqueous alkaline solutions of parent preparations to pH's ranging from 9.0 to 4.0 at temperatures between ambient and 80°C. The resulting precipitates will be redissolved in aqueous solution (volume at pH 7.5 minimized subject to complete dissolution) and thoroughly desalted (ultrafiltration with a 500 nominal molecular weight cutoff membrane) prior to freeze-drying.

The individual molecular components comprising the lignin preparations associate with one another very strongly in a well-defined (apparently stoichiometric) way. The extent to which this occurs is dependent upon pH and temperature. As the pH is reduced, the net charges on the components (which are phenolic in nature) are progressively neutralized. The temperature, on the other hand, influences the chemical equilibria that characterize the assembly of the associated complexes from the individual components.

During the precipitation of the lignin fractions, the complexes separate out preferentially, tending to leave the discrete components behind in solution. Consequently the work described here will identify the optimum conditions where precipitation from solution can yield preparations in which contamination from individual molecular species is minimized.

Other lignin derivative fractions will be obtained by ultrafiltering aqueous solutions of parent preparations at pH's between 11.5 and 7.5 using membranes with nominal molecular weight cutoff ranging from 10,000 to 200,000. Before freeze-drying, the solutions containing the species retained by the respective membranes will be adjusted to pH 7.5 and exhaustively desalted. (It should be mentioned that ultrafiltration of the wheat straw Organosolv lignins will require a suitable cosolvent such as methanol.)

Because it determines the charge densities on the constituent lignin species, the pH affects not only the relative proportions present of associated complexes and individual components, but also the sizes that the complexes can attain. Consequently ultrafiltration at different pH's will facilitate the isolation of fractions characterized by systematic variations in composition of the individual molecular components from which the complexes are assembled.

The permeabilities of the membranes will be selected so as to allow complete removal of the individual components from the complexes that are retained. Hereby a series of lignin fractions will be secured which differ according to the sizes of the constituent complexes and, therefore, the proportions of the higher and lower molecular weight component subsets from which they are composed.

A.3. *Budget.*
    a. Amount budgeted: $38,600
    b. Balance: $ 0

A.4. *Timeline for products/tasks.* July 91   Jan 92   June 92   Jan 93   June 93

Precipitation: pH and   . . . .
temperature dependence

Ultrafiltration: membrane   . . . .
and pH dependence

A.5. *Status.* The kraft process remains the method of choice for converting wood chips industrially into pulp for making paper. Large quantities of byproduct lignins are dissolved in the resulting "black liquor"; these represent (apart from the inorganic salts and carbohydrates) a broad range of degraded lignin polymer products with respect to their macromolecular properties and extent of physicochemical changes occurring during the pulping process.

The isolation and purification techniques described below have been developed with the goal of (i) understanding what byproduct lignin fractions could be potentially useful for making lignin-based plastics, and (ii) devising a well-defined approach with a high level of reproducibility for isolating preparative quantities of purified and characterized byproduct lignin raw material for fabricating lignin-based plastics with the highest possible lignin contents and appropriate mechanical properties.

The parent kraft lignin preparation predominantly used in making lignin-based plastic materials was isolated by acidification of an industrial "black liquor" that had been produced from Jack pine (*Pinus banksiana*) by the Boise Cascade Corporation (International Falls, Minnesota). The black liquor was diluted with HPLC grade water (7.3-fold) and the resulting solution filtered through a VWR 617 paper to remove residual fibrous material. Then, under vigorous stirring, the solution was acidified to pH 3.0 with aqueous 0.5 M H_2SO_4 (added from a buret at a rate of 1 drop per 10-15 s). The precipitation process was interrupted twice, at pH 11.0 and pH 8.5 respectively (before precipitation of lignin occurred), to remove colloidally suspended sulfur by centrifugation in a Beckman J-6B machine for 30 min. at 4200 rpm.

The kraft lignin precipitate that subsequently separated at pH 3.0 was isolated by centrifugation for 30 min. at 4200 rpm and then washed three times by consecutively resuspending in water acidified to pH 3.0 and centrifuging (using dilute aqueous H_2SO_4 for the first two washes and dilute aqueous HCl for the third). Whenever centrifugation failed to secure all of the solid kraft lignin present, the remaining suspension was basified to pH 8.5 and the clear solution rapidly reacidified to pH 3.0. Recentrifugation thereupon typically effected complete separation of the precipitate formed. From the original supernatant as well as from each supernatant wash solution, a 10 mL portion was set aside for

determining the mass balance, while the rest was designated for disposal. Finally, the various samples of kraft lignin precipitate were suspended together in a suitable volume (*ca.* 500 mL) of HPLC grade water and the mixture basified (aqueous 0.1 M NaOH) to pH 8.5. The resulting solution was then centrifuged for 30 min. at 4200 rpm to remove the last traces of colloidally suspended sulfur.

The substantial amount of inorganic salt occluded by the precipitate was then removed by ultrafiltration techniques (Amicon model 2000 high output 2 L teflon coated cell connected to a model RS 12 teflon coated 12 L reservoir) with a YC05 500 nominal molecular weight cutoff membrane, using high purity grade water (in a 10-fold greater volume). The resulting sample was distributed among an appropriate number of flasks for freeze-drying.

The overall mass balances were determined from the ultraviolet absorbance at 280 nm of the respective solutions made up so as to contain 0.1 M NaOH. The yield of the highly purified Jack pine kraft lignin obtained from the isolation procedure was 68.7%. The corresponding yield of aspen kraft lignin (from industrial black liquor supplied by the Potlatch Corporation, Cloquet, Minnesota) was quite comparable, *viz.* 66.4%, although here the final ultrafiltration step through a 500 nominal molecular weight cutoff membrane was omitted.

A similar approach was employed in isolating Jack pine kraft lignin fractions that are successively separated during the progressive acidification of the industrial black liquor. Here 220 mL of industrial kraft black liquor was diluted to 1600 mL with HPLC grade water and the resulting solution was again filtered through a VWR 617 paper to remove residual fibrous materials. A 20 mL sample was set aside for a subsequent mass balance determination by ultraviolet spectrophotometry. With vigorous stirring the diluted black liquor (pH 12.14) was acidified with 0.5 M aqueous H_2SO_4 added from a buret at a rate of 1 drop per 10-15 seconds. At pH 11.0 the solution was centrifuged for 4 h to remove small amounts of impurities. It was found that no precipitation occurs until pH 5.30. The solution (containing suspended solids) was successively centrifuged overnight at pH's from 5.30 to 3.60 in 0.10 pH intervals until separation of the respective precipitates was complete. No further precipitation below pH 3.60 was observed under these circumstances.

Each fraction was suspended in HPLC grade water and redissolved by basifying to pH 8.50. The solutions were centrifuged for 1 h in a Beckman J2-21 machine at 20,000 rpm to remove any sulfur liberated during the acidification of the black liquor and then they were frozen immediately for freeze-drying. The yields of the kraft lignin fractions obtained from the fractional acid precipitation are listed in Table I. Taken together, the fractions represented 77.5% of the total dissolved lignin in black liquor.

Table I

Kraft Lignin Yields Fractionally Precipitated
During Progressive Acidification of Black Liquor from Jack Pine

pH	%kraft lignin
5.30	1.29
5.20	3.08
5.10	3.75
5.00	5.54
4.90	8.46
4.80	10.31
4.70	25.38
4.60	11.19
4.50	8.93
4.40	6.14
4.30	4.95
4.20	3.41
4.10	2.71
4.00	1.98
3.90	1.46
3.70	0.97
3.60	0.45

The isolated Jack pine kraft lignin preparations comprise individual molecular components that associate with one another very strongly in a well-defined (apparently stoichiometric) way. The effect of reversible intermolecular association between kraft lignin species may readily be detected through the effects of pH and temperature. The average molecular weights steadily increase with time at sample concentrations greater than 100 gL^{-1} in aqueous alkaline solution with pH falling within narrow range immediately above the effective pK_a of the component phenoxide moieties (1). Dissociation, on the other hand, is observed at kraft lignin concentrations lower than 1 gL^{-1} in aqueous 0.10 M NaOH (1). The temperature influences the chemical equilibria and rates of reversion that characterize the assembly of the associated complexes from the individual components.

Accordingly a set of kraft lignin samples differing only in degree of association between the constituent species was secured by the following methods. Associated preparations were isolated from 160 gL^{-1} solutions of the Jack pine kraft lignin with 1.0 M ionic strength containing 0.40 M NaOH after incubation for periods ranging between 92.5 and 1220 h Upon dilution with water by a factor of *ca.* 25, the respective solutions, which were characterized by progressively increasing degrees of association between the kraft lignin components present, were acidified to pH 7.5 with aqueous HCl prior to freeze-drying. On the other hand, incubation of 0.10 gL^{-1} Jack pine kraft lignin solutions in aqueous 0.10 M NaOH for periods from 93.3 to 1301.3 h reduced the degree of association between the constituent species. As before the solutions were acidified to pH 7.5 with aqueous hydrochloric acid prior to freeze-drying. Ultimately five associated and four dissociated lignin preparations were isolated quantitatively and subsequently desalted by ultrafiltration (*vide supra*).

The development of convenient methods for isolation, purification and fractionation of lignins suitable for fabricating plastics has been the subject of continuous evaluation and modification in regard to possible industrial application. Precipitation as well as ultrafiltration techniques are simple methods applicable on a large scale. The lignin preparations produced thereby have been successfully used to produce cohesive materials with plastic properties (see section C.5).

The kraft delignification process, which gives rise to industrial "black liquor" (*vide supra*), represents a relatively strong chemical treatment of wood material and, as such, has a substantial effect on the degree of polymerization and the structure of lignin and its purity in terms of residual covalently bonded carbohydrates. Extensively modified lignin components that retain no memory of the native polymeric structure, as well as significant proportions of lignin-carbohydrate residues, derived mostly from hemicelluloses, could adversely affect the integrity of lignin-based plastics sheets. Therefore, two additional laboratory protocols were used to purify the lignin samples:

(i) Acid treatment of isolated Jack pine kraft lignin preparations was explored as a means of cleaving all remaining covalent bonds to the carbohydrate residues. Thus the parent Jack pine kraft lignin preparation (2.22 gL^{-1}) was refluxed for

15 h in trifluoroacetic acid:dioxane:water (5.13:2.85:1), whereafter the solvent components were removed under reduced pressure. During the process there was a tendency for the kraft lignin species to begin precipitating from solution so that some new interunit covalent bonds could have been formed between previously separate components. The conditions described above had been adjusted so as to avoid precipitation, but it is likely that some covalent modification of the lignin components, other than just the removal of mono- and oligosaccharidic fragments, still took place.

The residual kraft lignin sample was dissolved (1.18 gL^{-1}) in aqueous 0.10 M NaOH and allowed to stand in solution for 72 h. Upon 12.75-fold dilution in water, the solution was acidified with aqueous hydrochloric acid to pH 7.5 and ultrafiltration initiated with a YM5 5000 nominal molecular weight cutoff membrane. However, the kraft lignin sample began to show signs of precipitation not long after ultrafiltration was begun. The solution was basified to pH 10.0 and the process continued. After its volume had become 4.5-fold smaller than that of the original solution at pH 10.0, the retentate was washed with 40 L high purity water, concentrated and freeze-dried (pH 7.6).

(ii) Fractionation of lignins through Sephadex LH-20 gel with aqueous 35% dioxane in the presence of a localized salt band (initially containing 0.325 M NaOH) was employed to remove lignin components unable to participate in association/dissociation processes (see section B.5). However, industrially chromatography is not usually practicable and so ultrafiltration techniques were investigated as plausible alternatives for achieving the same result. Accordingly, using ultrafiltration membranes consecutively in declining order of their nominal molecular weight cutoffs between 100,000 and 500 (Amicon YM100, YM30, YM 10 and YC05), Jack pine kraft lignin was fractionated in such a way that the permeate from each particular step was (after concentration and adjustment of pH to 8.5) used as the starting solution for the next, while all retentates were kept (their final pH's varying between 7.5 and 7.8) for freeze-drying. The final samples were characterized with respect to their molecular weight distributions using size-exclusion chromatography (Sephadex G100/aqueous 0.10 M NaOH). Experiment has confirmed the feasibility of fractionating kraft lignin samples in this way providing that adequate reproducibility in experimental conditions can be maintained. A particular concern involves the performance characteristics of the membrane during any pressure fluctuation in the middle of the ultrafiltration process. For instance, releasing and subsequently restoring the pressure, when refilling the reservoir with additional sample solution or solvent, causes a change in the operational pore-size of the membrane owing to relaxation of the solute concentration polarization at its surface.

Another question concerns the incremental differences in molecular weight cutoff between consecutive membranes commercially available for ultrafiltration. These differences are typically so broad as to preclude acquisition of fractions with low polydispersity. Furthermore, the effective cutoff of each membrane, as reflected in the identities of the components comprising retentate

and permeate, is algebraically far from a step function; consequently there is considerable overlap in the ranges of the molecular weight distributions characterizing successive pairs of ultrafiltered fractions.

The use of ultrafiltration membranes individually has divulged an interesting result with regard to the composition of the kraft lignin fractions retained at pH 8.5. In the case of the 100,000 nominal molecular weight cutoff membrane, a bimodal distribution of high and intermediate-to-low molecular weight species in aqueous 0.10 M NaOH characterizes the kraft lignin fraction retained at pH 8.5. Such marked bimodality is not evident, however, in the retentates from the 30,000 and 10,000 nominal molecular weight cutoff membranes. This result confirms that, under favorable conditions, association between high molecular weight kraft lignin species and a complementary subset of smaller individual components takes place in a well-defined (non-random) manner. The underlying intermolecular interactions play a central role in maintaining the integrity and cohesiveness of solid lignin-based plastic materials (see section C.5).

References.
(1) Dutta, S.; Garver, T.M., Jr.; Sarkanen, S. *ACS Symp. Ser.* **1989**, *No. 397*, 155-176.

A.6. *Benefits.* Through methods which would be economically practicable on an industrial scale, a range of purified lignin fractions will become available for comparison with preparations previously established as having correct compositions for fabricating coherent plastic sheets.

B. **Analysis of purified lignin fractions.**

B.1. *Narrative.* The proportions of macromolecular complexes and individual components, their compatibility in regard to mutual interaction, and the frequencies of relevant chemical (functional) groups will be determined for the purified lignin fractions.

B.2. *Procedures.* The proportions of macromolecular complexes and individual components in the lignin fractions will be deduced from the corresponding molecular weight distributions disclosed by (size-exclusion chromatographic) Sephadex G100/aqueous 0.10 M NaOH elution profiles. The profiles will be calibrated by means of ultracentrifuge sedimentation equilibrium measurements. The resulting molecular weight distributions will depict the relative proportions of associated and discrete species under conditions comparable to those in the industrial liquors from which the preparations were originally isolated.

The compatibility of the constituent species with extensive intermolecular association will be investigated through HPSEC (high performance size-exclusion

chromatography) employing 10^6 Å or 10^7 Å pore-size poly(styrene-divinylbenzene)/DMF (dimethylformamide). Such analyses will be performed with both acetylated/methylated and underivatized samples.

Detailed studies have established that these experimental conditions yield results which can be interpreted reliably. A limited number (~ 5) of distinguishable species with very large hydrodynamic volumes are typically observed. Their populations are related to the molecular weight distributions encountered in aqueous alkaline solutions. The proportions of these highly associated species will determine the composition, and thus the mechanical properties, of the lignin-based plastic sheets themselves. An important utility of the molecular size distributions characterizing the preparations in DMF is that no individual components should be evident; if any remain, corrective measures must be taken in the fractionation procedures (subsection II A.2) through which they are obtained.

The original approach devised in the program manager's laboratories for preparing samples to be cast into plastic sheets involves chromatographic fractionation with Sephadex LH20/aqueous 35% dioxane. Although accumulation of adequate quantities of fractions by these means is extremely laborious, the resulting preparations have been quite well characterized; consequently they will be employed as analytical standards for comparative purposes.

Functional group frequencies (specifically the ratios of aliphatic hydroxyl, aromatic hydroxyl and methoxyl, and carboxylic acid groups) will be determined by ^{13}C NMR (nuclear magnetic resonance —— with gated proton decoupling) of suitably derivatized (acetylated/methylated) lignin fractions. Derivatization will be carried out by treatment with acetic anhydride/pyridine and diazomethane in successive stages. Quantitative recovery of the acetylated/methylated sample is more difficult in the case of polydisperse lignin samples than for small organic molecules, but a successful protocol has been developed which is suitable for routine application.

The functional group frequencies will be compared with those found in the standard analytical samples prepared chromatographically by elution with aqueous 35% dioxane through Sephadex LH20 (*vide supra*). A central concern here will be that carboxylic acids are completely absent: such functionalities are confined to components which have been chemically modified so drastically that they can no longer interact productively with the majority of the species present.

B.3. *Budget.*
- a. Amount budgeted: $42,100
- b. Balance: $ 0

B.4. *Timeline for products/tasks.* July 91 Jan 92 June 92 Jan 93 June 93

Chromatographic analyses   . . . .

Functional group determinations   . . . .

B.5. *Status.* Making plastic materials containing high percentages of byproduct lignins, which has now been successfully accomplished in the context of this project, requires careful characterization of the overall formulation so that improvements in the mechanical properties of the final products can be achieved in a predictable fashion and fabrication conditions can be reliably devised for future industrial application. The proportions of macromolecular complexes and individual components in the lignin preparations, their compatibility in regard to mutual intermolecular interactions, and the frequencies of the relevant chemical (functional) groups are particularly important in this connection. Size-exclusion chromatography has been employed to determine the proportions of macromolecular complexes and individual components in the kraft lignin samples from the corresponding molecular weight distributions disclosed by elution profiles under carefully chosen solution conditions. The profiles were calibrated in absolute terms by means of ultracentrifuge sedimentation equilibrium measurements (*vide infra*).

Upon elution with carbonate-free aqueous 0.10 M NaOH through Sephadex G100, the parent kraft lignin preparation exhibited the profile depicted in Figure 1A, which represents complete recovery of the solute. Under such conditions, the distribution of species comprises associated macromolecular complexes and individual components in the higher and lower molecular weight regions of the profile, respectively (1, 2). Nine fractions were selected from the overall molecular weight distribution and re-eluted twice through the same column system prior to absolute molecular weight determination (*vide infra*). The resulting profiles of these paucidisperse fractions are shown in Figure 1B to approximate reasonably well to Gaussian shapes. The kraft lignin molecular weight calibration curve deduced from ultracentrifuge sedimentation analyses of the fractions is depicted in Figure 2. The graph itself is compiled from a plot of log $\overline{M}_w$ *vs.* $V_{R,max}$ (the relative retention volume at the peak of the profile for each fraction). In regard to the parent kraft lignin preparation, the calibration curve is only applicable to $\overline{M}_w$'s below 50,000.

The compatibility of the constituent species with extensive intermolecular association was investigated through high performance size exclusion chromatography (HPSEC). The acetylated methylated kraft lignin derivative was eluted through a (600 × 7.5 mm) TSK-Gel®G7000-H6 10^7 Å pore-size poly(styrene-divinylbenzene) column using dimethylformamide (DMF) as solvent, whereupon the profile that was generated (representing 80% recovery of solute species from 0.0034 mg loadings) displayed the form depicted in Figure 3A. Paucidisperse acetylated methylated kraft lignin fractions from the profile were allocated to absolute molecular weight determinations using the analytical ultracentrifuge without re-elution through the column system.
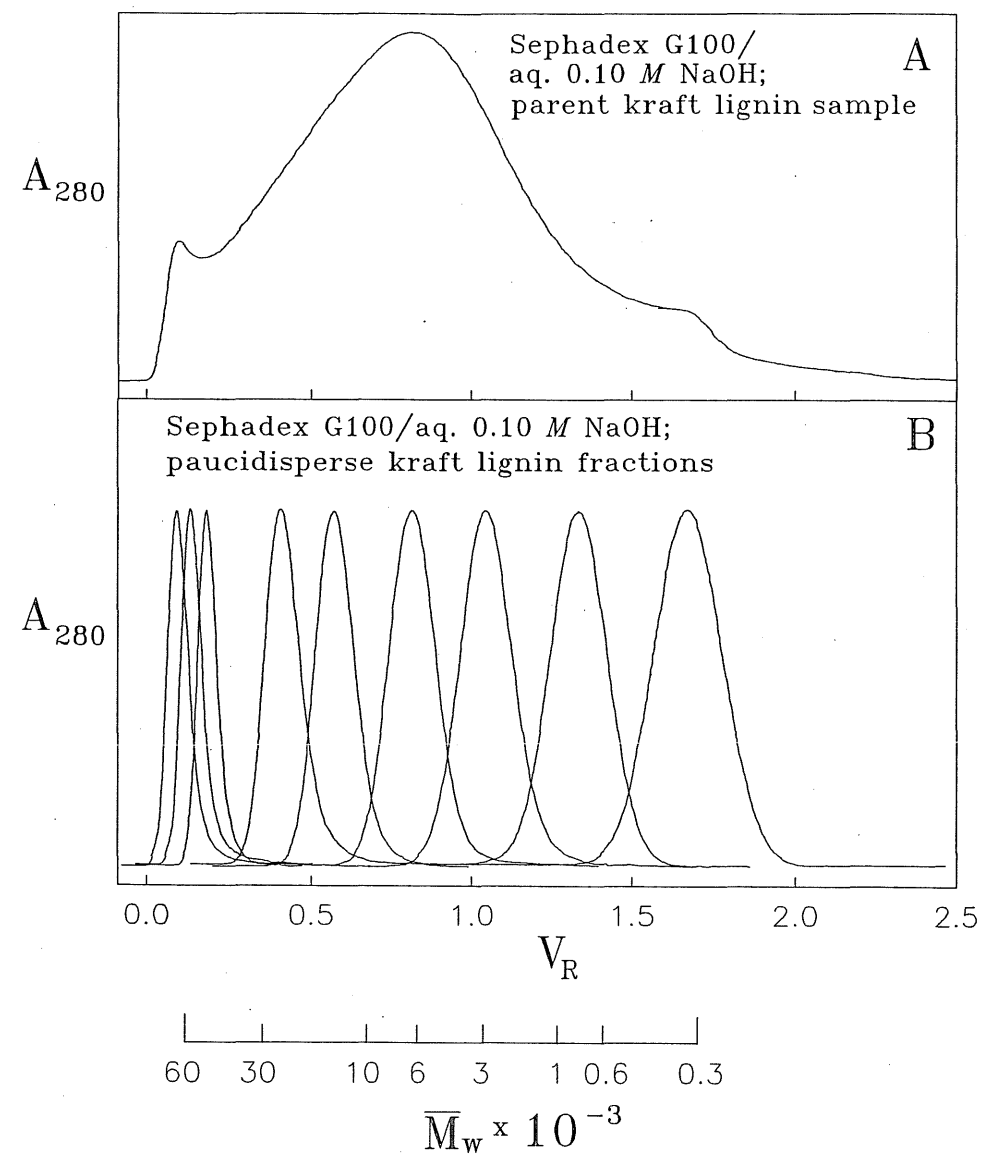
Fig. 1. (A) Kraft lignin sample from Jack pine and (B) paucidisperse fractions size-exclusion chromatographically produced from parent preparation. Elution profiles in aqueous 0.10 M NaOH from Sephadex G100 monitored at 280 nm; weight-average molecular weights of paucidisperse fractions deduced from sedimentation equilibrium analyses.
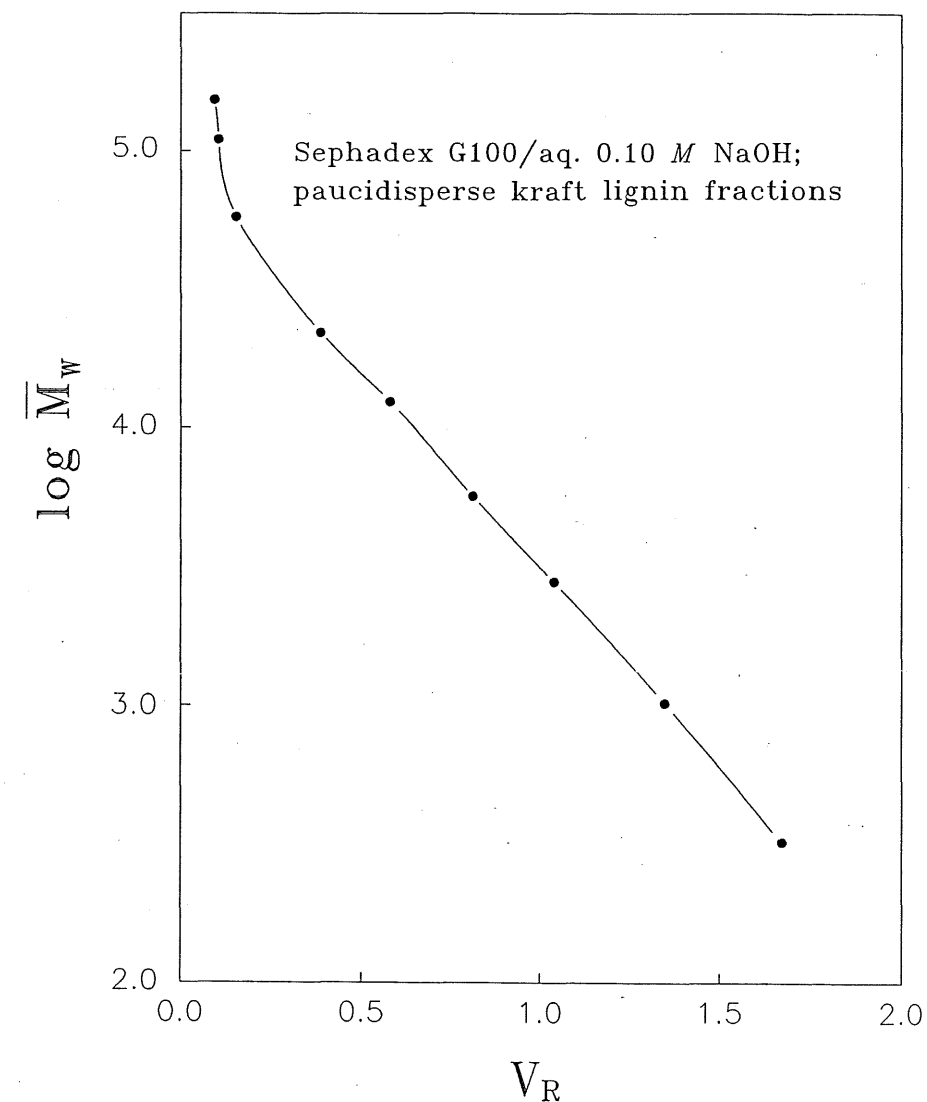

Fig. 2. Semilogarithmic plot of weight-average molecular weight $vs.$ relative retention volume for paucidisperse kraft lignin fractions eluted from Sephadex G100 with aqueous 0.10 M NaOH.
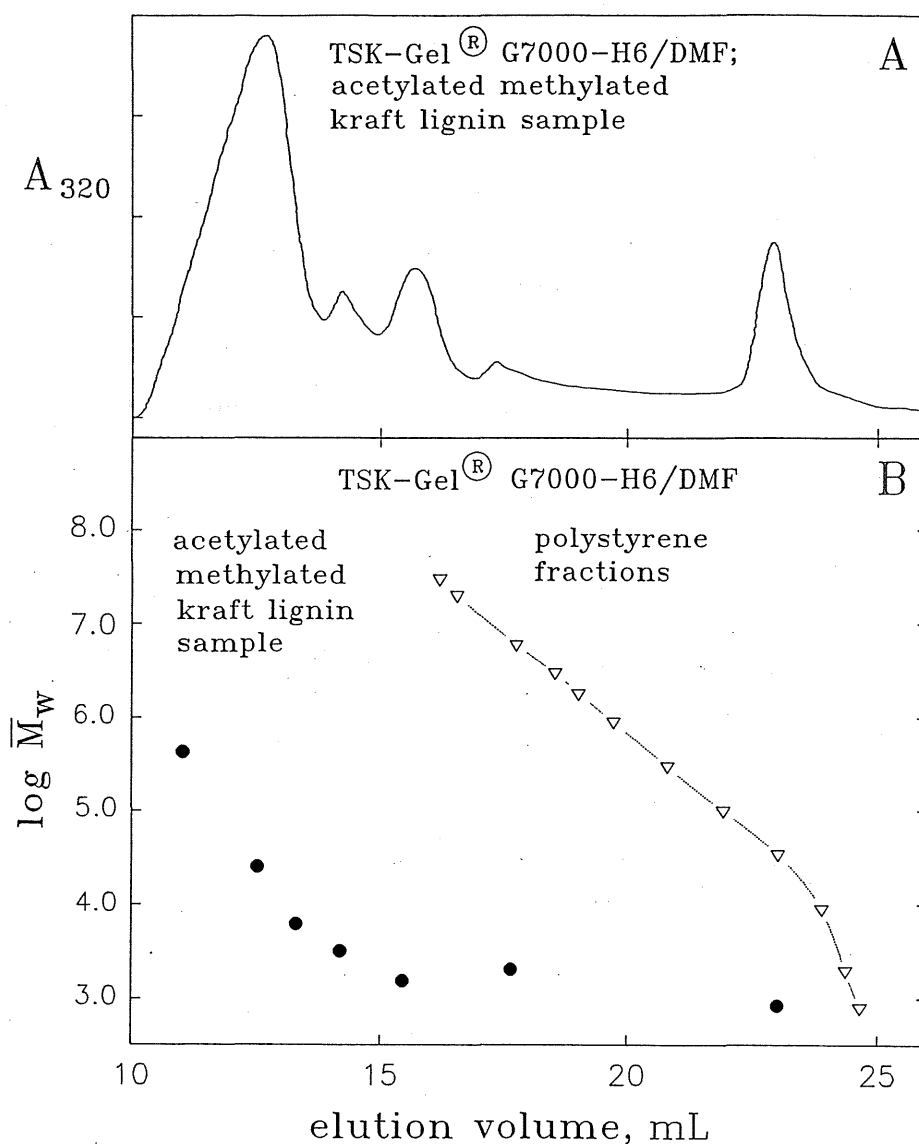
Fig. 3. (A) Acetylated methylated kraft lignin derivative. Elution profile in DMF from TSK-Gel°G7000-H6 column monitored at 320 nm; (B) corresponding semilogarithmic plot of weight-average molecular weight *vs.* elution volume (deduced from sedimentation equilibrium analyses) with polystyrene calibration curve for same chromatographic system.

The calibration curve deduced from ultracentrifuge sedimentation equilibrium analyses of these fractions is compared in Figure 3B with the corresponding plot for standard polystyrenes based on the molecular weight data provided by the suppliers (Polymer Laboratories, Inc., Polysciences, Inc., and the Pressure Chemical Company). It is evident that the distribution of acetylated methylated kraft lignin species in DMF extends to much higher molecular weights (Figure 3B) than the upper bound of the range encompassed by the underivatized kraft lignin preparation in aqueous 0.10 M NaOH (Figure 2). Clearly, associated macromolecular kraft lignin complexes persist in DMF without the agency of hydrogen-bonded interactions between the individual molecular components. A limited number of distinguishable species with very large hydrodynamic volumes is typically observed (3). The proportions of these highly associated species are expected to determine the configuration and thus the mechanical properties of the lignin-based plastic sheets themselves. Based on these findings, the use of DMF as a solvent or a component in a solvent mixture (to prompt formation associated complexes, which would presumably enhance the mechanical properties of the final products) and modification of the lignin samples by acetylation and methylation (to suppress solubility of the final products in aqueous solutions) has been examined in the context of casting lignin-based plastics (see section C.5).

Perhaps the most remarkable aspect of the results summarized in Figure 3B lies in the striking differences between the calibration curves for the polystyrenes and the acetylated methylated kraft lignin sample. For instance, at an elution volume around 15.0 mL in the HPSEC calibration curve, the acetylated methylated kraft lignin species exhibit molecular weights which are lower than those for polystyrenes by a factor of more than 50,000! Clearly calibration of size-exclusion chromatographic columns by non-lignin polymers in order to determine molecular weight distributions for lignin samples (a common practice, unfortunately, in the field of lignin chemistry) may lead to drastic errors.

Absolute molecular weight determinations using ultracentrifugal sedimentation equilibrium analyses has thus become unavoidable in the field of lignin chemistry. Significant differences in the hydrodynamic behavior of lignin derivative components isolated from natural sources and lignin model compounds as well as synthetic polymers under the same solution conditions preclude the use of the latter in attempts at characterizing the former (*vide supra*). Accordingly, here paucidisperse acetylated methylated and underivatized kraft lignin fractions (*vide supra*) were adopted for absolute molecular weight determinations at 8 × 10^{-3} gL^{-1} concentrations in DMF and aqueous 0.10 M NaOH, respectively, using the Beckman Optima XL-A analytical ultracentrifuge. The partial specific volumes of the solute species (0.744 cm^{3}g^{-1}) and densities of solvent or solution were measured with a Paar 60/602 digital density meter. The sedimentation curves were scanned at two wavelengths (280 and 320 nm) after equilibrium had been reached at more than one suitable rotor speed. The effective baseline at 600 nm was subtracted from each set of sedimentation equilibrium data in order to correct for any optical defects that might have been present in the cell assemblies.
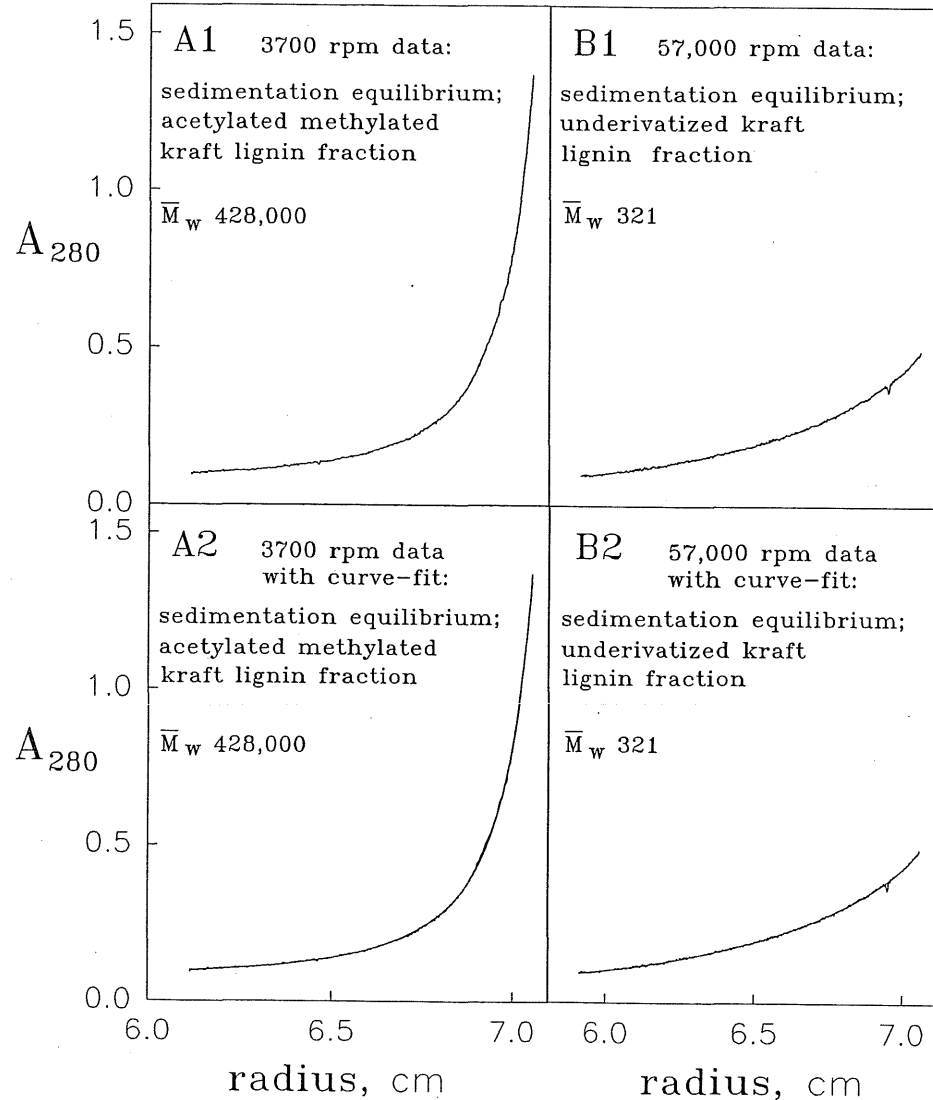
Fig. 4. Sedimentation equilibrium analyses of (A) acetylated methylated and (B) underivatized kraft lignin fractions. (1) Variation of solute concentration with radial distance from center of rotation monitored in Beckman Optima XL-A ultracentrifuge; (2) curve-fit to data points achieved by sum of exponential terms describing ideal solute species.

The resulting plots of absorbance *versus* radial distance from the center of rotation are exemplified in Figures 4A1 and 4B1.

The concentrations of kraft lignin species were so low that ideal behavior could, with reasonable confidence, be expected to prevail. Thus, using SigmaPlot®5.0 (Jandel Scientific, San Rafael, California), the sets of sedimentation equilibrium data for the paucidisperse acetylated methylated and underivatized kraft lignin fractions were successfully curve-fitted to functions comprising sums of exponential terms that describe the theoretically expected ideal sedimentation behavior for individual molecular components. In no case were more than four individual terms required for the fits of unprecedented accuracy that were achieved. These are exemplified in Figures 4A2 and 4B2. The areas under the component exponential curves confirmed that the total mass of solute species observed at equilibrium never differed by more than 1% from that present before the sedimentation process had begun.

The weight-average molecular weights, $\overline{M}_w$, calculated directly from the individual molecular weights in the respective terms of the curve-fitting expressions were, to all intents and purposes, identical to those computed by integrating the weight-average molecular weights, M_{wr}, deduced at every radial point along the respective solution columns in the ultracentrifugal cell assemblies. Furthermore the z-average molecular weights, $\overline{M}_z$, exhibited far less scatter than those calculated previously by curve-fitting with orthogonal polynomials (4).

The practical implementation of such an approach to analyzing sedimentation equilibrium data has not been previously realized and reported. In regard to the high sensitivity of the calculated molecular weights to the precision of the curve-fit, the protocol represents a very significant advance in the field of sedimentation equilibrium analysis.

It has been found (see section A.5) that the associative and dissociative processes taking place between lignin derivative species in solution depend on the prevailing conditions (pH, solvent, temperature, ionic strength, *etc*.). Lignins isolated from the main byproduct of a pulp mill (*e.g.* Jack pine kraft lignin isolated from black liquor) include species both able and unable to participate in these processes according to the extent of chemical modification that occurs during the delignification process. Extensive depolymerization and chemical change of the lignin macromolecule can reach a point where all memory of the original structural information is lost. Under such circumstances, the specific intermolecular interactions that govern the well-defined associative processes among the lignin derivative species have disappeared.

It has been supposed that a profitable device for fabricating cohesive lignin-based polymeric materials may be found in using kraft lignin fractions constituted exclusively from molecular components capable of interacting with one another in a well-defined way. Elution through Sephadex LH20 under specific conditions with aqueous 35% dioxane represents one approach to securing such fractions. Here the following protocol was used. A 2.0 *M* ionic strength localized salt band (NaCl dissolved in aqueous 35% dioxane) was introduced onto the column

ahead of the Jack pine kraft lignin preparation in aqueous 35% dioxane made basic with 0.325 M NaOH. Under these circumstances elution with aqueous 35% dioxane through Sephadex LH20 should routinely engender the segregation of the kraft lignin species into a subset of associated complexes appearing essentially at the void volume followed by the remaining components eluting immediately after the salt band (3). Under the solution conditions prevailing in the region of the localized salt band, association of the individual lignin components and dissociation of associated kraft lignin complexes occur on a time scale roughly comparable to the rate of elution through the chromatographic column. The kraft lignin species are also reversibly adsorbed onto the Sephadex LH20 packing material through a process that is favored by high ionic strengths and lower pH's, but those which have managed to diffuse through the salt band can behave in a more purely size-exclusion chromatographic way as far as their elution from the column is concerned. Thus, when the flow rate is faster and the pH near neutrality, only the more extensively assembled macromolecular kraft lignin complexes with large hydrodynamic volumes have the opportunity of diffusing through the salt band and gathering in the leading chromatographic peak.

The ability of such lignin fractions to become organized within domains embodying a high degree of intermolecular registration could enhance the mechanical properties of the ensuing lignin based plastics (see section C.5); confirmation has been forthcoming from the results of fabricating plastic materials from lignin preparations with different degrees of association. Lignin-based plastics have indeed been successfully cast for mechanical testing purposes in teflon molds of approximate dimension 3" × 3". The process has been carried out in a vacuum oven and the conditions varied with respect to temperature, pressure and the actual fabrication technique itself (see section C.5). An Instron model 4206-002 apparatus was used to determine stress-strain behavior and Young's modulus for the final plastic sheets. For each test, a separate piece with dimensions of 0.5" × 2.0" was cut from the parent sheet with regard for its homogeneity and thickness. The measurements were carried out at two crosshead speeds in each case (0.01 and 0.04 inch per minute, respectively) at ambient temperature (23°C). The strength properties of these plastics, with 85% unmodified lignin contents, were found to be comparable to the best materials previously fabricated elsewhere through extensive chemical crosslinking of lignin components——which themselves ultimately contributed only 30-40% to the final formulation.

References.
(1) Dutta, S.; Garver, T.M., Jr.; Sarkanen, S. *ACS Symp. Ser.* **1989**, *No 397*, 155-176.
(2) Sarkanen, S.; Teller, D.C.; Stevens, C.R.; McCarthy, J.L. *Macromolecules* **1984**, *17*, 2588-2597.
(3) Dutta, S.; Sarkanen, S. *Mat. Res. Soc. Symp. Proc.* **1990**, *197*, 31-39.
(4) Sarkanen, S.; Teller, D.C.; Abramowski, E.; McCarthy, J.L. *Macromolecules* **1982**, *15*, 1098-1104.

B.6. *Benefits.* Hereby the compositions of the purified lignin fractions can be compared directly with standard formulations developed under the auspices of work funded by LCMR during FY 90-91. The more elaborate analytical framework will facilitate an adequate measure of understanding about the fractionation procedures employed in pursuit of Objective A, owing to earlier fundamental studies conducted in the program manager's laboratories with support from NSF and USDA.

C. **Testing of lignin-based plastic sheets**

C.1. *Narrative.* Plastic sheets will be fabricated from the most promising lignin fractions and their mechanical properties measured. The first stage will be initiated in a search for additive components that could facilitate injection molding of lignin-based plastic parts.

C.2. *Procedures.* Plastic sheets will be cast from concentrated solutions of lignin fractions in suitable solvents or solvent mixtures. This solvent casting procedure will be carried out with 1.0 x 3.0 cm glass molds in a vacuum oven. The inertness of the lignin-based materials will be examined towards aqueous acidic and basic conditions, and selected nonaqueous solvents. The mechanical properties of the most promising plastic sheets will be determined by documenting their uniaxial stress-strain behavior and measuring their tensile strength using an Instron testing machine (crosshead speed to be optimized from 1 mm/min.).

It should be pointed out that solvent casting of the lignin-based plastic sheets is not itself likely to be suitable for industrial implementation. The work proposed here is focused upon the discovery of industrially applicable methods for securing byproduct lignin preparations which have component compositions compatible with the fabrication of coherent lignin-based materials. Thus solvent casting of plastic sheets is adequate for determining whether the primary objective has been achieved.

As far as industrial manufacturing processes are concerned, however, injection molding of lignin-based plastic parts represents the final goal of the entire research and development effort being envisioned. This ultimate stage in the contemplated work constitutes a project in its own right; separate funding will be sought at the appropriate time in the future from the U.S. Department of Energy for bringing the overall lignin-based plastics program to fruition (see section IV below).

Injection molding presupposes that the lignin-based materials will flow at elevated temperatures. Such behavior will require introduction into the formulation of small quantities of components that act like plasticizers. The first step in the quest will involve a search for low molecular weight compounds which, when present at threshold levels, sharply reduce the viscosity of concentrated lignin-containing solutions. Some compelling examples have been

reported in the literature (for example: Yaropolov, N.S.; Tishchenko, D.V. *Zh. Prikl. Khim.* **1970**, *43*, 1120-6; 1354-8), but more extensive studies will be needed to ensure a successful outcome from this approach. Certainly formulations incorporating promising low molecular weight compounds must be scrutinized analytically along lines similar to those described in subsection II B.2.

Although injection molding of lignin-based materials remains beyond the scope of the presently proposed work, exploratory viscosimetric studies will be carried out as probes for the preliminary identification of additive components that could be employed in developing the technology. When a promising result is obtained, access will be arranged to a small injection molding apparatus located in the laboratories of one of the program manager's colleagues at Virginia Polytechnic Institute and State University.

In the event that any of the lignin-based materials prove to be excessively brittle, the problem can be rectified in a straightforward manner. A search will be mounted for compatible elastomeric components that can be blended with the formulations in question. Such a procedure can be applied equally well to materials formed by solvent casting and injection molding.

C.3. *Budget.*
   a. Amount budgeted: $19,300
   b. Balance: $ 0

C.4. *Timeline for products/tasks.* July 91   Jan 92   June 92   Jan 93   June 93

Mechanical testing   . . . .
Viscosimetric studies   . . . .

C.5. *Status.* Plastic materials with high lignin contents (85% for the strongest samples) have been successfully fabricated from the most promising lignin fractions and their mechanical strengths have been measured. Casting conditions were investigated in the following consecutive stages of development:

(i) Development of a reproducible laboratory casting technique in regard to identifying the necessary conditions.

(ii) Casting lignin-based polymeric materials from solvents and solvent mixtures in the absence of additional blend components, but investigating the effect of low molecular weight compounds as possible plasticizers.

(iii) Casting lignin-based plastics with other polymeric materials as blend components at the lowest possible concentrations in the most promising solvents or solvent mixtures identified previously (*vide supra*).

For the first series of castings, glass molds (1.0×3.0 cm^2) were used. However, these assemblies proved unsuitable because of leakage of the casting solution into the joints between the glass components and interfering interfacial interactions between the lignin components and the surfaces of the molds.

Accordingly, teflon sheets were chosen and successfully fashioned into suitable forms as molds. The only remaining problem was to ensure that the bottom of the teflon mold would remain planar; attachment with a suitable adhesive to the surface of a metal sheet provided an adequate solution. The surfaces of the teflon mold were cleaned with soap, water, acetone, and methanol in that order, whereafter the casting itself was carried out in a vacuum oven. The temperature and pressure were selected according to:

(a) the solvent or solvent mixture employed (paying particular attention to preferential evaporation of one component in a mixture or premature attainment of boiling point);

(b) the original viscosity of the solution (with attendant problems arising from entrapped bubbles);

(c) control of evaporation rate so as to ensure homogeneity in the residual solid materials.

The casting technique had an important effect upon the quality of the final product; basically two approaches were employed: casting the whole volume of solution at one time, or casting in successive layers, additional solution being introduced only after the solvent from the previous portion had evaporated. The correct choice from among these alternatives prevented inhomogeneities in the final material as well as spontaneous fracturing of the lignin-based sheet. Exemplification of the necessity of using the layering technique is provided by the case where fast solvent evaporation occurs from the surface of a relatively deep lignin solution. Under such conditions a thin solid membrane is formed on the liquid surface that blocks escape of the solvent trapped underneath. Concomitantly, the slow contraction in the volume of the entrapped solution leads to serious stresses in the film on the top. Whether or not fully-fledged fractures are formed, one or more large cavities are inevitably found in the body of the solid material that is ultimately formed. On the other hand, the layering technique routinely resulted in homogeneous material without fractures.

Casting from solvents or solvent mixtures with and without potential plasticizers. The first step in fabricating lignin-based polymeric materials was the identification of suitable solvents or solvent mixtures for dissolving the samples and fractions prepared. The initial investigations followed an old idea (1) suggesting that the ability of solvents or solvent mixtures to dissolve a variety of lignin derivatives is the best when the corresponding Hildebrand solubility parameters approach values around 11. Altogether 58 different solvents were tested individually as well as in mixtures. In the case of solvent mixtures, the components were chosen in such a way that complete miscibility prevailed; otherwise they were preliminarily classified according to whether the Hildebrand solubility parameters were above or below 10 in magnitude. The idea of using solvent mixtures for casting always presents a potential problem from the point of view of preferential evaporation of one of the participating components: the lignin preparation may well be insoluble in the solvent that remains behind. In

such a case, obviously, a cohesive lignin-based polymeric material cannot be formed. Thus the most desirable solvent mixtures might have been azeotropes, the compositions of which would not change during evaporation. The solvent combination should have been composed of miscible low boiling organic liquids with low viscosity, which would have been capable of dissolving the lignin preparations at high concentrations (200 gL^{-1}). Of course, the solvent components should have been chemically inert with respect to one another and the lignin sample itself.

Solubilities in individual solvents as well as in solvent mixtures were evaluated after ultrasonication and, if necessary, incubation for 20 h followed by further ultrasonication. The results of extensive experimentation led to the two following conclusions: the Hildebrand solubility parameter is not a reliable criterion, even as a provisional guide; tabulated azeotropes were incompatible with high solubilities of kraft lignin preparations.

The initial tests were carried out with the parent Jack pine kraft lignin preparation at 5 gL^{-1} concentrations followed by higher concentrations when appropriate. It was found that the vast majority of the individual solvents were poor regardless of the magnitudes of their Hildebrand solubility parameters, even though solubility *tended* to be better in solvents with parameters above 10. The kraft lignin preparations were found to be fully soluble in ethylene glycol, acetic anhydride, glycerol, water, dimethylformamide and dimethylsulfoxide. However, addition of small quantities of water (mostly less than 1%, but in some cases up to 20%) to many solvents that alone were quite poor resulted in complete solubility for the kraft lignin preparations. This was observed with *t*-butanol, dioxane, acetone, ethanol, 2-methoxyethanol, 2-(2'-ethoxyethoxy)ethanol, *iso*-propanol, pyrrolidine, 1,2-dimethoxyethanol, pyridine and 2,6-lutidine.

The following solvent mixtures also dissolved the parent Jack pine kraft lignin preparation either partially (>50%) or completely: ethyl chloroacetate and dioxane; *n*-butanol and 2-(2'-ethoxyethoxy)ethanol; pyridine and tetrachloroethylene; acetone and nitrobenzene; methanol and benzene, chloroform, dioxane, acetone, acetonitrile, 2-methoxyethanol, methylene chloride, tetrachloroethylene, or tetrahydrofuran, respectively; carbon disulfide and pyridine or acetic anhydride; 2-methoxyethanol and chlorobenzene, chloroform, dioxane, acetone, acetonitrile, cyclohexane, toluene, nitromethane, nitroethane, or nitrobenzene, respectively. These include solvent combinations capable of forming azeotropic mixtures, but not in proportions compatible with complete dissolution of the Jack pine kraft lignin preparations. Generally speaking the presence in the solvent mixture of 2-methoxyethanol (methylcellosolve), methanol, pyrrolidine, 2-ethoxyethanol (ethylcellosolve), or 2-(2'-ethoxyethoxy)ethanol enhanced solubility to the greatest extent. Again, addition of 1-10% water in certain cases engendered complete solubility for the purified kraft lignin preparations even though the latter were no longer soluble in water alone. Based on the results obtained for the parent Jack pine kraft lignin, the most promising solvents and solvent mixtures were used with various series of Jack pine kraft

lignin samples derived from the parent preparation (after association, dissociation and treatment with acid, respectively) by different techniques (primarily Sephadex LH20 chromatography and ultrafiltration; see sections A.5 and B.5).

The fabrication of lignin-based polymeric materials followed an approach adopted for solvent casting that can be described in a series of simple steps: dissolution of the lignin derivative sample in a suitable solvent or solvent mixture (routinely 1:1 v/v unless otherwise indicated; for the sake of consistency in making comparisons, the concentrations of the kraft lignin fractions were 10 gL^{-1}); introduction of the resulting solutions into suitable molds in 1 mL portions (at this stage all work was carried out with 2 to 5 cm^2 molds fashioned from teflon sheet); and then removal of the solvent by evaporation under variously optimized conditions (samples were transferred into a vacuum oven, which was then flushed with nitrogen, evacuated and heated for specified periods of time ranging between 2 h and 95 h at temperatures and pressures varying from ambient to 100°C and 0" to 30" Hg, respectively; the final stage always involved 1 h exposure to 100°C at 30" Hg after all solvent had evaporated). The outcomes of the casting procedures were judged by the material remaining in the mold in terms of its cohesiveness, the density of visible fractures, glossy or mat surface appearance and (for the most promising cases) mechanical response characteristics as well as solubility in water. The differences among the materials produced from the various kraft lignin samples were of particular interest.

Generally speaking, the first stage in the research culminated in the successful fabrication of cohesive sheets of lignin-based polymeric materials from underivatized kraft lignin fractions. This remarkable outcome afforded an encouraging reason for additional research dedicated to improving their mechanical properties. The most consistently promising results were obtained with the Jack pine kraft lignin fractions isolated by chromatographic elution through Sephadex LH20 with aqueous 35% dioxane in the presence of a localized high ionic strength salt band (see section B.5), namely the subsets of species in the bands emerging from the column before the salt band. The materials that were cohesive sustained their integrity in the face of deformation through bending and application of local pressure.

For comparative purposes, attempts were also made to cast lignin-based polymeric materials from kraft lignin fractions obtained by ultrafiltration through a 5000 nominal molecular weight cutoff membrane: such a procedure could potentially mimic Sephadex LH20 chromatography in terms of its outcome. One example of a cohesive material was actually secured from these fractions. However, conditions for ultrafiltration have not yet been established that can duplicate the chromatographic results which have yielded the most promising kraft lignin fractions.

The mechanical properties of the lignin-based polymeric materials could reasonably be enhanced by creating bridges across the boundaries between adjacent domains of well-defined molecular arrangements which are presumably present in the solid. Glycerol and guaiacol were adopted for the purpose as small

molecules capable of interacting with the kraft lignin components through hydrogen-bonding and nonbonded orbital interactions, respectively. The addition, in turn, of 0.5% and 1.0% of both glycerol and guaiacol separately did facilitate the formation of cohesive polymeric material sheets in some cases. These lignin-based materials were capable of withstanding deformation by bending and application of local pressure, *i.e.* they were not brittle. However, in many other cases, the presence of glycerol as well as guaiacol in the casting solution appeared to influence the mechanical properties of the polymeric materials quite negatively. The density of fractures not only increased but the material also became more sensitive toward temperature and humidity changes.

Water solubility, as a basic criterion of environmental resistance in the final products, was investigated with all fabricated lignin-based polymeric materials, regardless of their quality. The weighed material was mixed with 20 mL water (HPLC grade) at ambient temperature (23°C) for exposure times of six weeks with occasional stirring. Thereafter the sample mixture was filtered through a medium-porosity fritted disc and the insoluble portion weighed. Concomitantly, the amount of soluble material was determined using UV spectrophotometry at 280 nm, the solutions being adjusted to 0.1 M NaOH for the purpose. The concentrations of dissolved kraft lignin were deduced from a UV calibration curve at the same wavelength.

From these studies it became evident that water solubility is not directly related to the qualities of the lignin-based polymeric materials but rather to the proportion of water employed in the original casting solution. Interestingly the presence of guaiacol as well as glycerol in the casting solutions (at 0.5% and 1.0% concentrations, respectively) reduced the water solubility of the lignin-based sheets, except when pyrrolidine had been used in the casting solution, where the reverse was the case.

The idea of using acetylated methylated kraft lignin fractions to eliminate any trace of water solubility in the fabricated polymeric materials became an obvious possibility. A series of associated and dissociated (see section A.5) Jack pine kraft lignin samples was acetylated and methylated (see section B.5) after desalting by ultrafiltration (Amicon YC05 membrane; see section A.5). Here chloroform and dimethylformamide (DMF) were used as solvents. Casting was carried out with a layering technique (*vide supra*). Kraft lignin solutions in chloroform afforded only one positive result but casting from DMF solutions led to compact (although hard and brittle) sheets in all cases. To confirm the stability of these sheets, the products were treated for a further 72 h in the vacuum oven at 40°C and 25" Hg. No change in appearance or consistency was observed at all. It was possible to separate the sheets from the teflon molds in cohesive form. The positive role of DMF as a solvent in the casting process is related to the extensive association that takes place between the lignin components even when hydrogen bonding is precluded (see section B.5).

Casting in the presence of other polymers. The brittleness of lignin-based polymeric materials as well as their tendency to become spontaneously fractured during or after the casting procedure do not favor industrial utilization of these materials as they stand. Introduction of other commercially available polymers at the lowest possible concentrations (as plasticizers) in blends was investigated to solve these problems. Accordingly, series of polymers were chosen in regard to their similarity in structure to the kraft lignin components and one of them, poly(4-vinyl phenol), was methylated using a standard procedure (dimethyl sulfate/aqueous 15% sodium hydroxide). Casting in DMF was carried out wherever possible, except when prohibited by low solubility on the part of the blending components whereupon other suitable solvents were selected. The solubility of poly(vinyl alcohol) as well as poly(ethylene-vinyl alcohol) was found to be poor in a number of the most common polymer solvents (*e.g.* dimethylsulfoxide, dioxane, ammonia, acetonitrile, tetrahydrofuran) and, surprisingly, in water too. Ultimately, pyridine and pyrrolidine were found to be suitable, coincidentally encouraging in relation to the previous results of casting from solutions in these solvents. Finally, the following polymer solutions were prepared for casting: PVAc, PMMA, PSMM, PEVAc, and PDMA in DMF; PVA, PEVA in pyrrolidine; PEVAc in chloroform; and PEVAc in DMF:chloroform (1:1).

Casting without a kraft lignin preparation always resulted in a cohesive sheet with no fractures. The concentration of each polymer, introduced into the casting solution containing kraft lignin, was at four levels, *viz.* 10%, 20%, 30% and 50% w/w with respect to the lignin sample. The casting conditions were generally set at 40°C and 10"-30" Hg using teflon 0.5×0.5 cm^2 molds containing *ca.* 1 mL sample volumes. A graduated layering technique seems to be the most successful for creating these blends. The main problem with the majority of experiments was incompatibility of the kraft lignin and the polymer chosen for the intended blend resulting in phase separation of the respective species. Only low concentrations of kraft lignin were homogeneously incorporated into the polymer sheets imparting to them a light brown color, while the remaining kraft lignin separated into its own morphologically characteristic form. However, several selected trials yielded interesting results in the form of homogeneous blended kraft lignin-polymer sheets.

Casting with poly(4-vinyl phenol) and the methylated derivative in DMF. PVP and the methylated derivative were introduced into the system respectively with underivatized and acetylated methylated kraft lignins in 10% (w/w) concentrations. Regardless of derivatization or degree of association, all castings resulted in brittle sheets with low densities of fractures.

Casting with PEVAc. Acetylated methylated as well as underivatized associated Jack pine kraft lignin preparations were cast with 28% (w/w) PEVAc from a 1:1 DMF:chloroform solvent mixture at 40°C and 10" Hg in a vacuum oven. While the casting with the underivatized lignin resulted in a brittle sheet with a high density of fractures, the acetylated methylated kraft lignin yielded a brittle but

cohesive sheet. Casting from chloroform alone resulted in phase separation so that DMF in some way enhances the compatibility of the kraft lignin with the poly(ethylene-vinyl acetate).

Casting with poly(ethylene-vinyl alcohol). PEVA was introduced into pyrrolidine solutions of acetylated methylated associated and dissociated Jack pine kraft lignins in a 50% (w/w) concentration. Casting in the vacuum oven at 40°C and 25" Hg resulted in cohesive sheets with limited elasticity. Under the microscope (40× magnification) no heterogeneity was visible.

Casting with poly(vinyl alcohol). Exactly the same concentrations, lignin preparations and casting conditions were used as in the previous case with poly(ethylene-vinyl alcohol). The experiments resulted in cohesive sheets with limited elasticity. No heterogeneities were observed under the microscope (40× magnification).

Casting with poly(N,N-dimethylacrylamide). PDMA (10% w/w) was introduced into DMF solutions of underivatized associated and dissociated kraft lignin samples. Castings were carried out again at 40°C and 25" Hg in a vacuum oven. Regardless of the degree of association or dissociation, brittle sheets with low densities of fractures were formed but no kraft lignin-polymer incompatibility within the sheets was observed.

Casting with a commercially available polymer emulsion (CAPE). A series of experiments was carried out with a commercially available aqueous polymer emulsion which itself gives cohesive sheets with plastic properties as a result of casting.

The experiment with an emulsion system was dedicated to investigating its compatibility with high kraft lignin concentrations and consequent creation of a homogeneous system yielding cohesive blends with plastic and thermoplastic properties after solvent evaporation. The pH of the CAPE after 4-fold dilution with high purity water was 6.05 (the pH of water itself was 6.68). Based on three independent determinations it was found that the solids content represented 45.1% of the original emulsion. Three different underivatized Jack pine kraft lignin preparations were used in the series of experiments with CAPE: that isolated by acid precipitation from black liquor and subsequently desalted by ultrafiltration (Amicon YC05 membrane); one associated for 1200 h and desalted by ultrafiltration; and one dissociated for 626 h and desalted by ultrafiltration. In an initial experiment, casting of a mixture of CAPE and the original Jack pine kraft lignin in a 1:1 weight ratio diluted 3-fold by water resulted in a cohesive sheet that was bendable and even foldable. Introduction of higher kraft lignin concentrations into the formulation required gradual addition of water with ultimate use of ultrasonication. So far the maximum successfully employed lignin concentration with respect to the total solids content has reached 85%. This represents a striking advance in regard to all previously reported results in this research area (2-11). Casting in a vacuum oven under a nitrogen atmosphere at 40°C and 25" Hg (with eventual annealing at 80°C and 25" Hg for 12 h in some cases) resulted in cohesive sheets with plastic properties that are bendable and

partially stretchable; after 6 week exposure to ambient conditions, these materials become harder and more brittle but modest elevation in temperature to about 40°C restores bendability and deformability. It was observed that the initial viscosity of the casting solution has a major influence on the material's ultimate properties; higher as well as lower viscosities lead to cracking and fracturing during casting.

Very interesting lignin-based polymeric materials were obtained with pyrrolidine instead of water in the previous experiment. CAPE (originally as emulsion) is completely soluble in pyrrolidine giving a viscous clear solution; dissolution occurs when a particular level of pyrrolidine has been added. Mixing of kraft lignin with CAPE in pyrrolidine requires an additional amount of pyrrolidine to maintain viscosity. As before the viscosity of the casting solution affects ultimate sheet quality. However, while with water alone the viscosity is critical within a relatively narrow range to obtain a cohesive material, in the case of pyrrolidine the upper limit of dilution is flexible and the results of casting depend on the ratio of pyrrolidine to other components. Here the range of additional pyrrolidine varied between the lowest concentration needed to obtain a castable viscous mixture and a 500% excess by volume. In general, increasing the pyrrolidine excess concentration changes the sheet quality from opaque with a glossy surface to translucent with a leathery appearance. Casting under the standard conditions in the vacuum oven (40°C, 25" Hg in a nitrogen atmosphere) took finally a much longer time in comparison with casting the water-based solution, extending to as much as two weeks. Even after a further two months of extended treatment in the vacuum oven under the same conditions, the sheets remained plastic and bendable at laboratory temperatures. However, the question of the residual presence of traces of pyrrolidine and its role in maintaining the mechanical properties of the final lignin-based materials has not been fully resolved.

Methylcellosolve (2-methoxyethanol) appeared as a possible replacement for pyrrolidine because of its easier removal from the casting solution and the similarity between the solubilities of CAPE in the two solvents. Unfortunately the gradual addition of methylcellosolve to CAPE resulted ultimately in phase separation of the emulsion components. The more general problem is the insolubility of kraft lignin at high concentrations in the only usable CAPE-methylcellosolve mixtures involving ratios between 1:2 and 1:3. Furthermore the addition of a 1:1 methylcellosolve:pyrrolidine mixture resulted in phase separation of kraft lignin from a formulation involving CAPE in the casting solution. Another possibility, the replacement of pyrrolidine with ammonia, was investigated, but without success. Experiments resulted in kraft lignin phase separation from the formulation during the casting process. Addition of methylcellosolve resulted in breakdown of the emulsion owing to the excess water originating from the aqueous ammonia: in the presence of methylcellosolve or pyrrolidine, no additional water over that originally present in CAPE can be tolerated.

Generally speaking, there was a visible difference in the color of the fabricated lignin-based materials that depended upon the degree of association of the Jack pine kraft lignin; dissociated starting materials led to lighter colors than more associated samples, but otherwise the surface appearance was very similar.

The approach successfully developed here was suitable for fabricating larger kraft lignin sheets correspondingly in larger teflon molds (4.5 × 4.5 cm²). The materials obtained were always easily removable from the mold so that the mechanical properties of the samples could be easily tested by standard methods. An Instron testing apparatus, model 4206 (Instron Corporation), was used for investigating the stress-strain behavior of the lignin-based polymeric materials (see Table II & Figures 5-7). For these purposes, pieces of average size 1.0 cm × 5.0 cm × 0.1 cm were prepared and tested at ambient temperature (23°C) and at two crosshead speeds (0.01 and 0.04 in./min.), in triplicate for each sample. The Young's moduli reported represent the average value of three independent measurements.

Table II
Strengths of Plastics Fabricated from Industrial
Byproduct Jack Pine Kraft Lignin Preparations*

Sample no.	Formulation	Crosshead speed (in./min.)	Young's modulus (GPa)
1.	Commercially available polymer emulsion (CAPE)	0.01	0.165
		0.04	0.241
2.	85% parent kraft lignin, 15% CAPE, water; final annealing at 80°C & 25" Hg for 12 h	0.01	0.798
		0.04	1.04
3.	85% parent kraft lignin, 15% CAPE, water; without annealing after casting	0.01	0.895
		0.04	1.01
4.	85% kraft lignin predissociated for 626 h, 15% CAPE, water	0.01	0.647
		0.04	0.721
5.	85% kraft lignin preassociated for 1200 h, 15% CAPE, water	0.01	1.03
		0.04	1.18
6.	85% parent kraft lignin, 15% CAPE, with minimum quantity of pyrrolidine	0.01	0.199
		0.04	0.224
7.	85% parent kraft lignin, 15% CAPE, with 5-fold excess pyrrolidine	0.01	0.132
		0.04	0.192

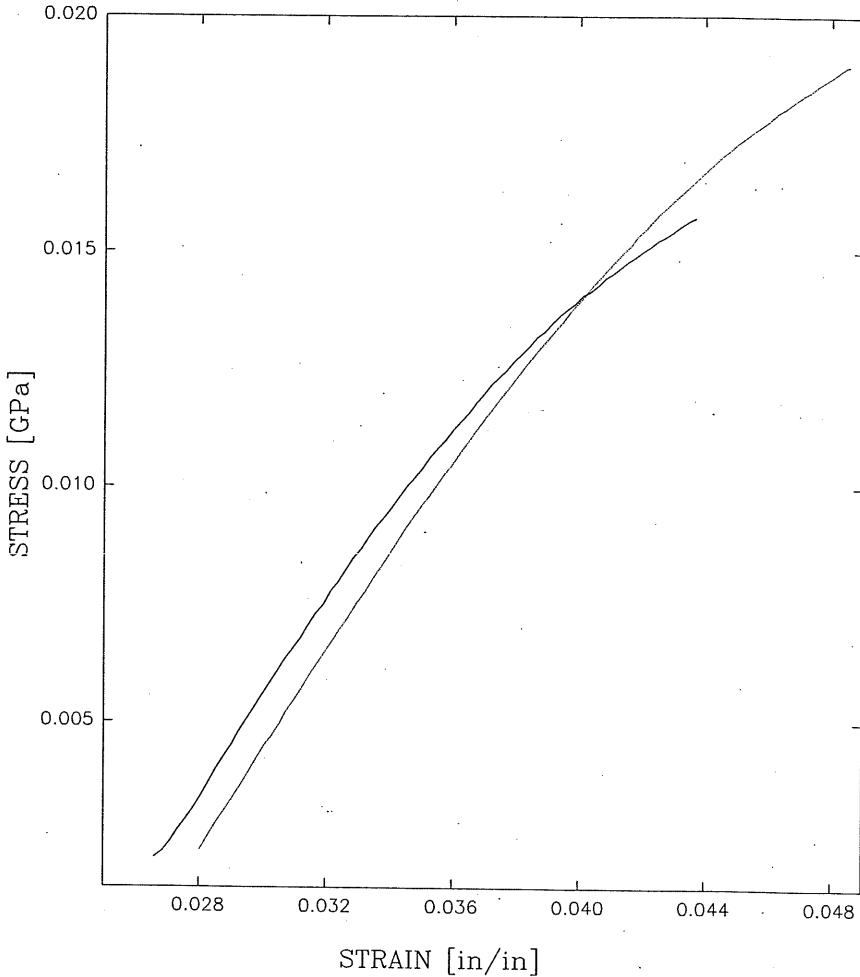*Casting conditions: 40°C, 25" Hg, nitrogen atmosphere.

Fig. 5. Stress-strain behavior of lignin-based polymeric materials; *solid line*: plastic cast from 85% parent kraft lignin and 15% CAPE in water alone followed by 12 h annealing at 80°C; *dotted line*: plastic cast from 85% parent kraft lignin and 15% CAPE in water alone without subsequent annealing.
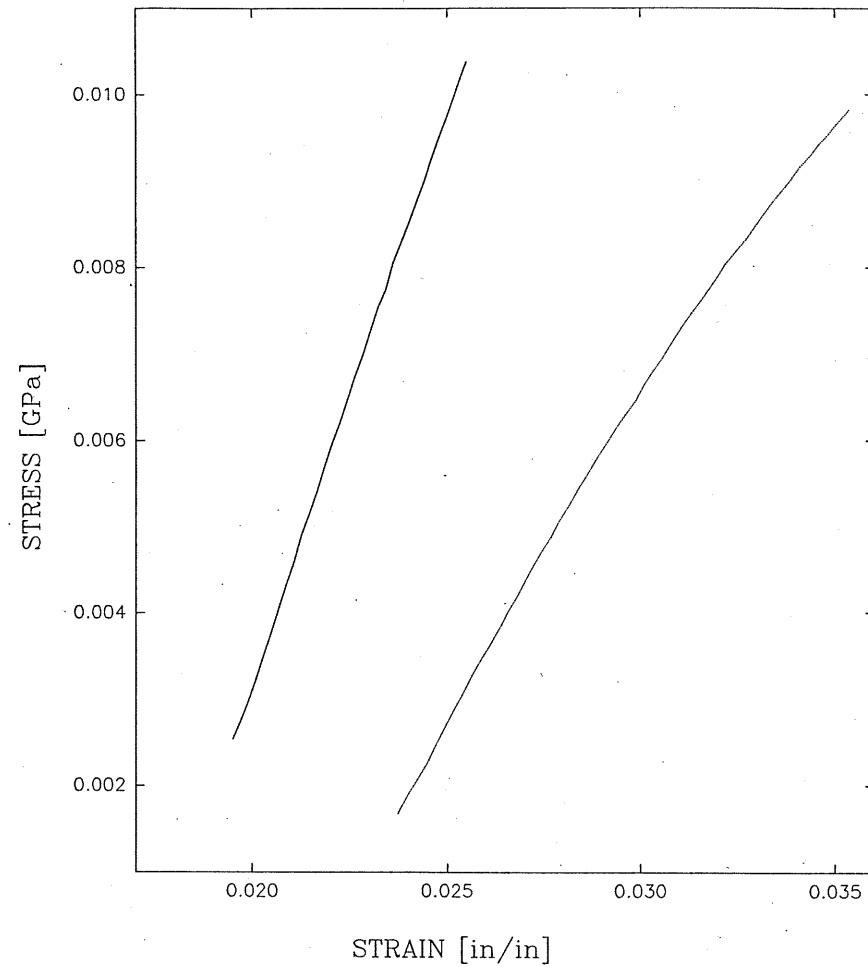
Fig. 6. Stress-strain behavior of lignin-based polymeric materials; *solid line*: plastic cast from 85% preassociated (1200 h) kraft lignin and 15% CAPE in water alone; *dotted line*: plastic cast from 85% predissociated (626 h) kraft lignin and 15% CAPE in water alone.
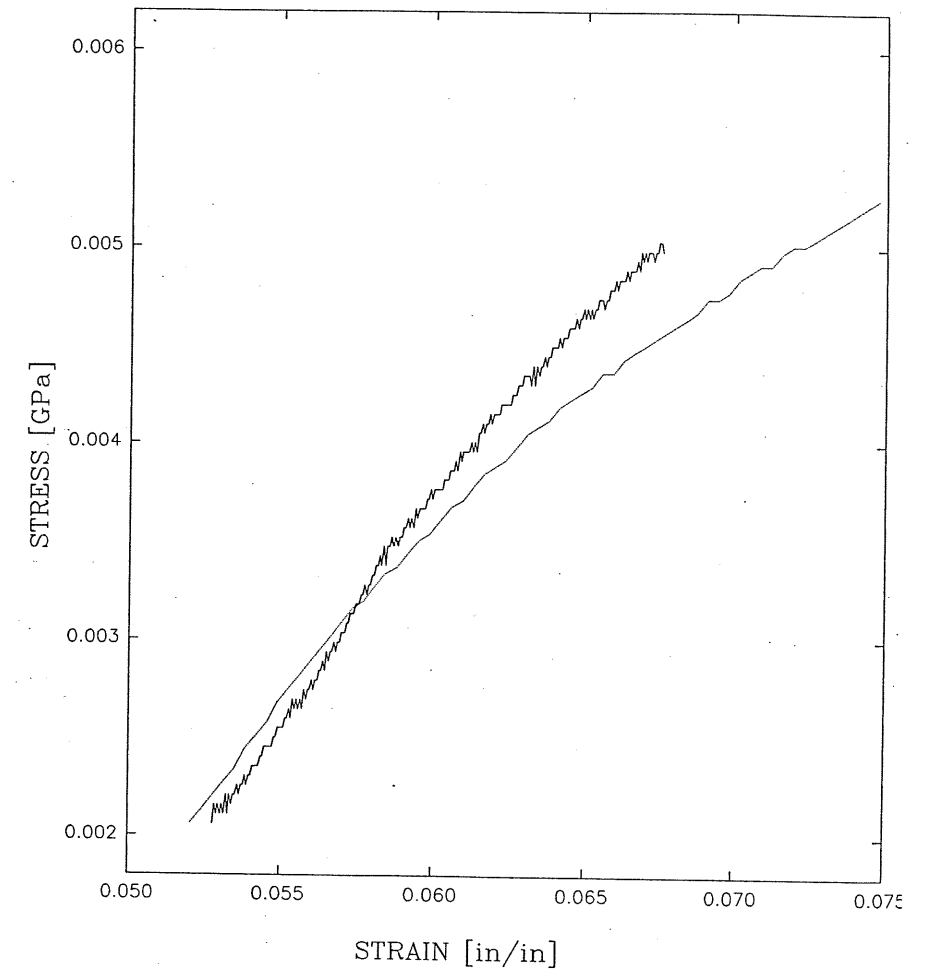

Fig. 7. Stress-strain behavior of lignin-based polymeric materials; *solid line*: plastic cast from 85% parent kraft lignin and 15% CAPE with minimum quantity of pyrrolidine; *dotted line*: plastic cast from 85% parent kraft lignin and 15% CAPE with 5-fold excess pyrrolidine.

It is important to emphasize that these plastics with 85% underivatized kraft lignin contents have strengths quite comparable to the best fabricated elsewhere by chemically crosslinking lignin components, but the previous materials optimally contained only 30-40% of the lignin derivative in the final formulation (2-11). The presence of pyrrolidine in the casting solution, when in excess, seems to have a deleterious effect upon the strength of the final material (Table II, samples 6 & 7), even when compared to pure CAPE alone. On the other hand, water-based casting solutions gave hard strong materials (Table II: *cf.* samples 2 & 3 with sample 1) regardless of prolonged exposure to elevated temperatures. The resulting strength depends directly on the degree of association of the kraft lignin preparation (Table II: *cf.* samples 4 & 5 with samples 2 & 3). These remarkable results represent the threshold of a new chapter in the field of biodegradable plastics from renewable resources. Of course much remains to be done, but the feasibility of producing strong materials from individual byproduct lignins with little or no chemical modification has, for the first time, been demonstrated.

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C.6. *Benefits.* The performance of the most promising lignin-based plastic sheets will hereby be established in terms of their strength properties, while the first step towards injection molding lignin-based plastic parts will have been initiated.

IV. Evaluation

The program can be viewed as having been successful if the procedures envisaged culminate in the fabrication of plastic sheets with reasonable mechanical properties from aspen kraft, Jack pine kraft and wheat straw Organosolv lignins. Such an accomplishment, which has not been previously realized, would represent a considerable return on the investment.

Longer term validation of the proposed work would be confirmed by substantial federal funding (*e.g.* from the Office of Industrial Programs, Conservation of Renewable Energy at DOE) for which the anticipated results would provide persuasive justification. Thus the program will have created the basis for bringing to the market place entirely new types of biodegradable plastics made from very cheap industrial byproducts and agricultural residues.

V. Context

A. More than 20 million tons of kraft lignins are produced annually in the United States by the pulping industry, and traditionally 99.9% of these aromatic polymeric byproducts have been used as fuel in the recovery furnace stages of pulp mills. However, as efforts are being made to maximize production, an increasing number of mills have become overloaded in their recovery operations. Already in 1989, the Potlatch Corporation in Cloquet, Minnesota, was shipping some excess kraft black liquor to be burned at International Falls, but it is expected that the Boise Cascade site will itself become recovery loaded by 1991. Similar circumstances have plagued numerous mills in the southeastern United States for many years. Thus the need to find economically worthwhile outlets for underutilized industrial byproduct lignins is becoming ever more acute.

The parallel exploitation of Organosolv lignins from agricultural residues represents an attractive adjunct to such a goal: the technological basis for pulping wheat straw, as an example, is already in place and requires only process optimization.

A compelling way of meeting the challenge lies in the development of lignin-based plastics. During the past decade at Virginia Polytechnic Institute & State University and the University of Detroit, substantial efforts have been mounted to employ lignin components either as extenders in polyurethanes, acrylics and epoxy resins or as grafting backbones for the attachment of other synthetic polymer sidechains. Of these, at least one option has shown signs of becoming commercially viable. Nevertheless, while they should be applauded,

these achievements have paid little direct attention to the inherent physicochemical properties of the lignin preparations themselves.

B. The contemplated research and development program is entirely different from any other currently under way elsewhere in the world. It recognizes at the outset that the majority of the molecular species which comprise lignin preparations tend to interact (*i.e.* associate) with one another very strongly. It is predicated upon devising simple and effective means for separating these species from all other components present that are structurally incompatible with extensive intermolecular association. Subsequent casting of the resulting lignin fractions will then produce polymeric materials incorporating broad domains of regularly disposed arrangements at the molecular level. The uniqueness of the proposed work lies in its intent to fabricate biodegradable lignin-based plastics with little or no *chemical* modification of the starting materials themselves.

C. The opportunities being embraced here have surfaced as a result of fundamental studies conducted in the program manager's laboratories with support from NSF (grant no. CBT-8412604 for investigating "Associative Interactions between Kraft Lignin Components") and USDA (grant no. 86 FSTY-9-0166 for the "Isolation and Characterization of Kraft Lignin Components"). The prior work disclosed some unprecedented findings about the physicochemical properties of a kraft lignin sample isolated from an industrial Douglas fir black liquor supplied by the Weyerhaeuser Company. It became evident that the assembly of macromolecular kraft lignin complexes occurs through successive interactions with individual molecular components in a specific order. Moreover, a fairly straightforward manipulation of chromatographic procedures led to a method for sequestering into a single fraction all those kraft lignin species capable of interacting productively with one another.

Thus an approach to fabricating lignin-based plastics successfully, without modifying the starting materials chemically, was implied. LCMR funding during the FY 90-91 biennium has provided the first opportunity for putting the idea into practice, and at the time of writing the results have shown clear signs of promise. It is anticipated that support from LCMR beyond the FY 92-93 biennium will not be necessary for securing more extensive funding from appropriate federal and industrial sources.

D. Biennial Budget System program title for FY 90-91:

Lignin-Based Eng. Plastics

Budget amount: $108,000

E. Biennial Budget System program title for FY 92-93:

Means for Producing Lignin-Based Plastics

VI. **Qualifications**

1. *Program Manager:* Simo Sarkanen

a. *Qualifications related to proposed work.*

1976 Ph.D., bio-organic chemistry, Department of Chemistry, University of Washington.

1977-80 Postdoctoral research associate, lignin chemistry, Department of Chemical Engineering, University of Washington.

1981-87 Assistant professor, wood chemistry, Department of Forest Products, University of Minnesota.

1987- Associate professor, wood chemistry, Department of Forest Products, University of Minnesota.

b. *Institutional affiliation.*   Department of Forest Products
University of Minnesota
specific specialization: lignin chemistry

c.1. *Summary of work accomplishments related to proposal.*

Since 1978, the program manager has been intensively engaged in studying the physicochemical behavior of lignin derivative preparations. By 1988, his contributions had received recognition to the point where he was invited to co-organize a symposium devoted to "Lignin——Properties and Materials" at the Third Chemical Congress of North America held in Toronto during June of that year. The participants included researchers from nine different countries, and the presentations resulted in the publication of a book (listed in subsection c.2 below) where two-thirds of the chapters deal with lignin-based plastics.

The program manager was subsequently asked to talk about the work being supported by LCMR during FY 90-91 at the Materials Research Society national meeting held in San Francisco during April 1990. The request came from Stanley Sobczynski, program manager in the Office of Industrial Programs, Conservation of Renewable Energy at DOE. The presentation resulted in the acceptance for publication of a refereed article (listed in subsection c.2 below) on the topic.

c.2. *Principal publications related to proposal.*

Lignin——Properties and Materials: Glasser, W.G., Sarkanen, S., Eds.; *ACS Symposium Series;* American Chemical Society: Washington, D.C., 1989, No. 397.

A New Emphasis in Strategies for Developing Lignin-Based Plastics: Dutta, S.; Sarkanen, S. In "Materials Interactions Relevant to the Pulp, Paper and Wood Industries"; Caulfield, D.F., Passaretti, J.D., Sobczynski, S.F., Eds.; Materials Research Society: Pittsburgh, 1990; pp 31-9.

2.   *Cooperators and Other Investigators:*

    Cooperators: not applicable

    Other investigators: Dr. Juraj Mlynár, research associate;
                                 Mr. Yan Li, graduate student;
                                 Mr. Wenshan Zhuang, graduate student.

VII.   Reporting Requirements

Semiannual status reports will be submitted not later than January 1, 1992, July 1, 1992, January 1, 1993, and a final status report by June 30, 1993.

1991 RESEARCH PROJECT ABSTRACT
For the period ending September 30, 1993
This project was supported by Oil Overcharge Money (MS 4.071)

Title: Means for Producing Lignin-Based Plastics
Program Manager: Simo Sarkanen
Organization: University of Minnesota, Department of Forest Products
Legal Citation: M.L. 91, Ch. 254, Art. 1, Sec. 14, Subd. 13(f)
Appropriation Amount: $100,000

STATEMENT of OBJECTIVES

The project was focused upon fabricating biodegradable plastics from surplus industrial lignins produced by mills in Minnesota during the chemical process of converting wood to pulp for making paper. It was necessary for these lignin-based plastics to have acceptable strength properties with little or no further chemical modification of the raw materials. Thus a commitment was made to develop entirely new kinds of biodegradable plastics using surplus industrial byproduct lignins derived from renewable wood resources in Minnesota.

RESULTS

Parent kraft lignin samples were isolated by acidifying pulp mill "black liquors". Subsequent fractionation and purification were accomplished by ultrafiltration, a process that can be employed on an industrial scale. The resulting lignin preparations were capable of being transformed by solvent casting into cohesive sheets, but such materials, if composed exclusively of lignin components, were very weak and brittle.

On the other hand, casting (from water alone) blends of chemically unmodified kraft lignin preparations (**85%**) with a commercially available polymer emulsion (15%) produced strong materials with Young's moduli around 1 GPa. *Nothing like it has ever before been achieved.* The strengths of these lignin-based plastics depended upon the degree of association between the lignin components present (*i.e.* the extent to which the individual molecular species had become assembled, through noncovalent interactions, into macromolecular complexes).

The new biodegradable plastics are as strong as the best lignin containing materials produced during the 1980's in other laboratories by means of (expensive) chemical crosslinking; however the optimum lignin contents in the previous formulations only fell between 30% and 40%.

PROJECT RESULTS USE and DISSEMINATION

The foregoing results have been described in the corresponding Final Status Report to the LCMR dated 9.30.93, but they have not otherwise been disseminated. The feasibility of fabricating strong biodegradable plastics containing high proportions of chemically unmodified industrial byproduct lignins has been demonstrated for the first time, but adequate patent coverage is needed if these new materials are to be brought to the market place. Such protection will require complete documentation of the fundamental basis for formulating successful blends. Thus a considerable amount of further work is necessary before more specific details can be disclosed to the community at large.