# STRUCTURE-PROPERTY RELATIONSHIPS IN POLYURETHANES FROM LIGNIN

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#### ABSTRACT

Lignin based polyurethane films were synthesized by solution casting from hydroxypropyl lignins and diisocyanates. Kraft and steam explosion lignin, hexamethylene diisocyanate (HDI) and tolylene diisocyanate (TDI), were used for the study. It was found necessary to use stoichiometric excess amounts of diisocyanates in the synthesis of the thermosetting polyurethanes. The investigation primarily addresses the effect of synthesis variables and soft segment incorporation on the thermal and mechanical properties.

The first part of the study examined the effect of lignin type, of diisocyanate type and of composition (NCO/OH ratio). Stoichiometric excess was found to cause a significant increase in the glass transition temperature. Use of HDI resulted in films with lower moduli as compared to TDI. NCO/OH stoichiometry variation had no noticeable effect on modulus or tensile strength.

In the second part of the study involving incorporation of soft segments, four polyethylene glycols were used. No soft segment phase in the network was detectable by differential scanning calorimetry or dynamic mechanical analysis. The glass transition temperature of lignin phase dropped by as much as 70°C for HDI and 115°C for TDI based polyurethanes with inclusion of glycols up to 25% of the polyol weight. The swelling tendencies showed an expected increase with glycol content. Effect on mechanical properties were more pronounced in HDI than in TDI based polyurethanes. The modulus and tensile strength decreased, and the ultimate strain values increased with polyethylene glycol content.

Last part of the study involved synthesis and characterization of kraft polyurethanes with polybutadiene glycol with functionality in excess of 2.0. The miscibility of this phase with hydroxypropyl lignin phase was found to be poor as observed by scanning electron microscopy. Glass transition temperature for the lignin phase increased with polybutadiene glycol content of the polyurethane in contrast to observations on polyethylene glycol modified polyurethanes. There were no significant improvements in tensile properties. The incompatibility of soft segments was seen to result in a more condensed lignin phase, and was thus found to be the major limitation in its applicability in modification of the network properties.

The study demonstrates the utility of concept of network modification in the synthesis lignin based thermosetting of polyurethanes. By proper choice of synthesis variables, and with the use of glycols of sufficient compatibility, significant improvements in properties can be realised in these polyurethanes.

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#### GLOSSARY OF TERMS

- DMA Dynamic Mechanical Analysis
- DSC Differential Scanning Calorimetry
- FT-IR Fourier Transform Infrared
- HDI Hexamethylene diisocyanate
- HPL Hydroxypropyl lignin
- IH Polyurethanes with steam explosion (lotech) lignin and HDI
- IT Polyurethanes with steam explosion (lotech) lignin and TDI
- KBH Polyurethanes with kraft lignin, polybutadiene glycol and HDI
- KBT Polyurethanes with kraft lignin, polybutadiene glycol and TDI
- KEH Polyurethanes with kraft lignin, polyethylene glycol and HDI
- KET Polyurethanes with kraft lignin, polyethylene glycol and TDI
- NMR Nuclear Magnetic Resonance
- SEM Scanning Electron Microscopy / Micrograph
- T Glass transition temperature

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#### Chapter I

#### INTRODUCTION

Energy and raw material shortages have renewed the interest in materials hitherto underutilized by reason of limitation in understanding of structure and consequent lack of process technologies. In this category lignin deserves a special mention as a 'polymeric' material produced by pulping processes, which currently finds its major use as fuel. Kraft lignin, in the black liquor of the kraft pulping process, is currently the major type of lignin produced in the United States.<sup>1</sup> Utilization alternatives include low molecular weight chemical feedstocks such as phenol, and an increasing number of polymeric products including adhesives, resins, antioxidants, dispersants, and elastomer (rubber) reinforcing agents.<sup>2</sup>

#### 1.1 OVERVIEW OF LIGNIN STRUCTURE

Much progress, though it is still far from complete, has been made in the past thirty years towards understanding the formation of this polymer. Present knowledge stems essentially from the work carried out by K. Freudenberg and his school at the University of Heidelberg. The current definition envisages lignin as polymer arising from enzymatic (peroxidase), dehydrogenative polymerization of three primary precursors: trans -coniferyl, trans-sinapyl and trans-p-coumaryl

alcohols.<sup>3</sup> The structures of these cinnamyl alcohols is given in Figure 1. Phenylpropane units are accepted as sole building blocks of lignins. The polymerization route involves several reactive (free radical) intermediates which couple in a random fashion producing a network containing a multitude of interunit linkages. These include several types of ether ( $\beta$ -O-4,  $\alpha$ -O-4 and 4-O-5) and carbon-carbon linkages. In addition there also exists a wide spectrum of functional groups in lignin influencing its character and properties.<sup>4</sup>

The structure however, is adequately understood to have become a subject of computer simulation efforts treating lignin as a statistical polymer.<sup>5-10</sup> A structure derived by computer simulation, which accounts for the results of all major chemical analyses, is illustrated in Figure 2. Kraft pulping leads to the hydrolysis of most of the alkyl-aryl ether linkages (except methoxy groups), liberating phenolic hydroxyls in the process and solubilising fragments of lignin.

#### 1.2 POLYURETHANES FROM LIGNIN

The applications of urethane polymers are increasing in the field of fibers, elastomers, foams and coatings.<sup>11</sup> These products are best known for their high tensile strength, load bearing capacity and resistance to abrasion. With a wide range of structural variations, end products have been made with diverse character and properties. Thermoplastic polyurethanes, moisture curing and two component solvent based systems, blocked isocyanates and prepolymers are some of the important industrial applications.



Figure 1: Structures of Lignin Precursors.



Figure 2: Computer Simulated Hardwood Lignin Structure (Glasser and Glasser<sup>8</sup>).

Various schemes to utilize lignin as a polyurethane base are available in the literature.<sup>12-19</sup> The primary impetus lies not only in its natural abundance and renewability, but also because it is one of the largest low value industrial byproducts. Isolated lignin has functionality in its primary and phenolic hydroxyls, which possess enough reactivity towards isocyanates<sup>14</sup> and thus has been investigated for use in polyurethane applications. All previous attempts, however, have suffered from a lack of characterization and stability of the formulation. In earlier studies potential use of lignin was viewed as an inexpensive inert filler and extender in polymeric products. In one example, Nichols<sup>12</sup> employed kraft lignin as a reinforcing agent in elastomeric compositions based on polyethers, polyester amides and polyalkylene glycols, and reported improved properties for the final elastomeric product by using oxidized kraft lignin instead of the unmodified form. This observation indicates that the presence of reactive groups in lignin makes it possible to incorporate lignin into the matrix of a polymeric material. This concept was later used by Mills<sup>13</sup> for abrasion-resistant rubber compositions. The method of production of such lignin reinforced rubber vulcanizates involved coprecipitation of lignin with rubber latex and treatment with an organic polyisocyanate. Moorer<sup>16</sup> and Santelli<sup>17</sup> in their methods to produce lignin polyurethane foams used straight chain glycols to improve the strength properties of the foams. In these cases however lignin has been used as a coreactant rather than as the primary network

component. These studies illustrated that the major limitation for the use of lignin in polymeric products concerns its polydisperse and multifunctional characteristics and also the differences in the reactivity of the groups. The synthesis of a more uniformly functional derivative should therefore assist in the preparation of a lignin based plastic. It has already been shown that the conversion of phenolic to aliphatic hydroxyls enables macromolecular lignin to be used as a polyol component in polyurethane foams.<sup>20</sup> Hydroxypropylation was identified as a suitable modification reaction for such purpose, and this has been the subject of extensive investigations.<sup>21–35</sup> The incorporation of these types of lignin derivatives as a sole hydroxy component in the production of polyurethanes remains to be demonstrated.

#### 1.3 STATEMENT OF OBJECTIVES

The objective of this study is to investigate the structure-property relationships in thermosetting polyurethanes based on lignin. Following are the specific goals of the study.

a. To explore the following structural variables influencing the properties of polyurethanes:

- 1. Lignin type.
- 2. Nature of the diisocyanate.
- 3. Crosslink density variations.

b. To examine the following modifications based on incorporation of soft segments on the properties of polyurethanes:

- 1. Polybutadiene glycol- compositional variations.
- 2. Polyethylene glycols- compositional variations.

- molecular weight variations.

c. To analyze the resulting solid state structure of lignin based polyurethanes by:

- 1. Differential Scanning Calorimetry.
- 2. Dynamic Mechanical Analysis.
- 3. Small Angle X-ray Scattering.
- 4. Scanning Electron Microscopy.

#### Chapter II

#### LITERATURE SURVEY

Properties of thermosetting polymers being dependent on network architecture, the understanding of structure-property relationships provides a valuable guide to alter the macromolecular properties. The importance of modifications in structure to improve perfomance of polymer relevant to application, has been realised not only in linear polymers, but also in network systems like epoxies of wide industrial utility. Grafting of rubbery particles with thermoplastic chains, or chemical attachment of rubbery systems through functional end groups, has been proven to provide the necessary means of translation of energy to rubbery region, thus reducing inherent brittleness of the system.

#### Effect of Microstructure on Polymer Properties

Perhaps, most of the knowledge of increasing toughness of polymeric materials in the production of elastomers has developed with the advent of linear segmented elastomers, particularly the thermoplastic polyurethanes.<sup>36-50</sup> A great number of studies have been carried out and reviews of the results are available.<sup>47</sup>,<sup>48</sup> Many studies on morphology of these segmented copolymers have attributed the toughness in these materials to soft and hard segment architecture. Evidence has been gathered with techniques such as small angle X-ray scattering, infrared spectroscopy, differential scanning calorimetry and dynamic mechanical analysis.

On the basis of progress made in understanding of structure at molecular level, it is now established that the combination of high modulus and strength originate from physical crosslinking or reinforcement caused by the hard segment domains dispersed in soft segment matrix. According to accepted terminology, hard segment means the diisocyanate and chain extender, and soft segment is derived from glycol. Physically crosslinked hard segments are imbedded in a rubbery matrix, resulting in high strength and modulus. It has been well established that the properties of thermoplastic polyurethane elastomers result from thermodyanamic incompatibility of the soft and hard segments, which lead to microphase separation, domain formation and the development of long range order in the hard segment domains.<sup>51\_53</sup> Polyurethane phase separation has been unequivocally shown to exist mainly in uncrosslinked thermoplastic types including some polycaprolactone glycol based polyurethanes.<sup>54</sup>,<sup>55</sup> Small angle X-ray scattering has been used as a qualitative method of confirmation of domain structure as inferred by other tests.<sup>56-57</sup> Additional information bearing on the domain structure has been obtained from infrared spectroscopy<sup>58</sup> which in polyether containing polyurethanes allows a direct estimate of distribution of the hydrogen bonded NHgroup between interurethane hydrogen bonding and hydrogen bonding to ether oxygen of the soft segments.<sup>59</sup>

On the other hand, there have been fewer number of studies on crosslinked polyurethane systems, most of them on structure-property

relationships.<sup>60-75</sup> Investigations on the effect of composition on domain morphology have been carried out on a limited scale in contrast to epoxies, which represent one of the widely studied network systems. Investigators in the field of epoxies have emphasized a view of the network essentially as a composite, with a high-crosslink-density phase less crosslinked matrix.<sup>76</sup> embedded in а Existence of such heterogeneity has been inferred from results of diverse investigations using techniques such as electron and optical microscopy, thermomechanical measurements, differential swelling and differential scanning calorimetry. In network polyurethanes, studies indicate that the existence of phase structure is subject to structural factors. Existence of crosslinks can restrain linear chains from assuming configurations necessary to produce a domain structure. Cooper and Tobolsky, <sup>63</sup> in studying changes in thermomechanical spectra on crosslinking linear thermoplastic elastomers, inferred that depending on the number and location of crosslinks, the domain structure can be maintained or destroyed. Wilkes et al. used the pulsed proton NMR technique<sup>77</sup> and small angle X-ray scattering<sup>78</sup> to study the existence and kinetics of domain formation in a series of polyester based polyurethanes. The urethanes were thermally crosslinked to different The differences between the extents with an organic peroxide. segmental mobility of the hard and soft phases was shown to decrease with crosslinking. Well aged samples with lower crosslinking showed higher phase separation as evidenced by higher intensity SAXS curves.

The greater segmental mobility in this case was also shown by greater departure from steady state upon thermal treatment and faster return on aging. These effects were attributed to the inability of the segments in crosslinked material to completely segregate into domains. Although advances in characterization of network structures are not comparable to linear systems, improvements in properties through modification have been sought. It has been realised that in the reinforcement of rigid network such as epoxy, there can be introduced in a controlled manner, structures with flexibility, to alter ultimate physical and mechanical properties.

#### Effect of Composition on Properties of Network Polyurethanes

In the field of polyurethane coatings and adhesives, there have been some studies on the effect of molecular structure of components and composition of the resin on the network properties. O'Shea<sup>79</sup> studied the behavior of thermoplastic polyurethanes based on poly (oxyethylene -oxypropylene) glycols by varying the NCO/OH ratio. A considerable difference in the development of hardness with quench time was observed. Quick hardness development for the ratio of 1.01 and very slow develpment for the ratio of 1.05 were noted and explained on the basis of kinetics of domain formation, drawing upon the theory of "demixing" proposed by Wilkes et al.<sup>80–82</sup> to account for the time dependent behavior of thermoplastic polyurethanes. Even though the crosslinking introduced by the variation of the NCO/OH ratio from 1.01 to 1.05 due to allophanate and biuret formation is low, it can exert significant influence on the demixing process and re-establishment of the domain morpholgy. Branching was considered to have a disruptive effect on chain alignment and establishment of hydrogen bonding thus slowing down the rate of formation of long range order and crystallinity which lead to the development of hardness in the cooling of the crystalline polymer. The DSC measurments on the samples prepared with various NCO/OH ratios showed a shift in the position and broadness of the hard segment crystallization exotherm. The peak becomes broader and appears at progressively lower temperature as the NCO/OH ratio is increased, an observation consistent with slower hardness development.

Guise et al.<sup>83</sup> investigated the properties of cast polyurethanes (crosslinked thermosets) prepared from  $poly - \varepsilon$ -caprolactone diols and hexamethylene diisocyanate (HDI) and tolylene diisocyanate (TDI). Polyurethanes were prepared by a one-step method and either polycaprolactone triol or trimethylpropane was used as a crosslinking The materials showed melting and glass transitions when agent. examined by differential scanning calorimetry and thermomechanical analysis. Decreasing the triol concentration or using less than the amount of diisocyanate was observed to facilitate stoichiometric crystallization apparently due to decreasing the extent of crosslinking. Replacing TDI by HDI had the same effect due to higher segmental mobility in the latter; it also shifted the  $T_a$  to lower temperatures.

However, in these formulations prepared with stoichiometric amounts of diisocyanates, the crosslink density (concentration of triol) had little effect on the glass transition temperature ( $T_g$ ). Also, the urethane group concentration usually increases  $T_g$  associated with hard segments. In this case it was difficult to separate the effect of diol molecular weight and urethane concentration, since increase in diol molecular weight is invariably accompanied by a reduction in the weight content of urethane groups in order to maintain stoichiometry. However, by comparison of polyurethanes from one particular diol molecular weight, it was concluded that  $T_g$  was more influenced by molecular weight of the diol than by urethane concentration. Though the invariance of  $T_g$  with urethane concentration has been taken as evidence for phase separation,<sup>54</sup> the applicability of that criteria in this case was doubtful due to low hard segment concentration.

Matsuda et al.<sup>\$\*</sup> studied the properties of polyurethane films having thermosetting properties. The polyurethane-urea-amines were based on polytetramethylene glycol (PTMG) and TDI with diethylene triamine (DTA) as crosslinking agent. Modulus, tensile strength and hardness increased as the molecular weight of PTMG increased. These were explained in terms of the increased crystallinity of the oxybutylene blocks.

In an effort to study the behavior of the polyurethane crosslink density the prepolymer /DTA ratio was varied from 0.8-0.95. The tensile strength of the heat cured film showed a maximum at the ratio of

0.83 indicating the balance between molecular weight of the polyurethane-urea-amine and chemical crosslinking was important. It is noted that as the ratio comes close to 1.0 the molecular weight is expected to increase. The crosslink density variation was also studied by varying TDI/PTMG ratio; the increase in physical and chemical crosslinks was found to increase the 100% modulus. The contribution by the increased aromaticity is also observed to be a factor. However, no systematic variation of strength was observed.

Hoffman<sup>\$5</sup> investigated the thermal and dynamic mechanical behavior of seven urethane adhesives based on poly (tetramethylene oxide), including some crosslinked systems with Q-quadrol as crosslinking agent. Hard segments containing this tetrafunctional chain extender showed strikingly different dynamic mechanical behavior as compared to those containing butanediol. The tetrafunctional quadrol extended the rubbery plateau beyond the melting point of the hard segments as expected, but also decreased the overall load bearing capacity of the hard segments causing the rubbery modulus of the crosslinked systems to be lower than the linear systems at temperatures below the hard segment melting transition. The melting of the hard segments caused only a slight change in modulus and the adhesive system maintained its integrity till the degradation temperature. The crosslinking also affected both the soft and hard segment transitions, slightly raising the temperature at which these occur.

#### Chapter III

#### MATERIALS AND METHODS

#### 3.1 MATERIALS

#### Lignins

- Kraft lignin: Commercial pine kraft lignin, isolated by acidification of kraft black liquor, was obtained from Westvaco, Charleston, SC, under the trade name INDULIN ATR-C1
- 2. Steam Explosion Lignin (lotech Lignin): Steam explosion lignin was supplied by lotech Corporation, Ottawa, Canada. The method of preparation involved extraction of steam exploded aspen chips with aqueous NaOH (0.4%), and this has been described by Marchessault et al.<sup>86</sup>

#### Isocyanates

Isocyanates used were hexamethylene diisocyanate (HDI) and 2,4-tolylene diisocyanate (TDI), practical grade by Eastman Kodak Company, Rochester, N.Y.

#### Polyethylene Glycols

Polyethylene glycols, of molecular weight 400, 600 and 1000 g/mol (Carbowax PEG 400, 600, and 1000, respectively), by Fisher Scientific Company, Fair Lawn, N.J. and of molecular weight 4000 g/mol, (Carbowax PEG 4000), by Union Carbide Corp., New York, N.Y. were used for the study.

#### Polybutadiene Glycol

Polybutadiene glycol (Poly bd R45-HT) used in this study, is a homopolymer of butadiene with an average molecular weight 2800 g/mol and functionality of 2.4-2.6. Hydroxyl content (0.83 meq/g) is predominantly allylic type. The microstructure has 60% trans-1,4, 20% cis-1,4 and 20% vinyl-1,2.<sup>87</sup> The resin was made available by ARCO Chemical Company, Philadelphia, Pa.

#### Hydroxypropyl Lignins

Solid lignins were reacted with propylene oxide in a closed, mechanically stirred stainless steel reactor with a glass lining. Hydroxypropyl lignins were prepared by anionic addition of propylene oxide using anhydrous potassium hydroxide the catalyst. The amount of the catalyst used for kraft and steam explosion lignins were 3.3 and 2.0% respectively, on weight basis. Tolylene was used as a suspending and heat transfer agent.

After sealing the reactor, the reaction mixture was heated to a control temperature of 200°C with vigorous stirring. Heat flow to the reactor was regulated in a such a way that after an initial overshoot, the temperature was maintained at 200°C throughout the reaction. As the reaction is exothermic, a typical run has a peak pressure stage in the immediate vicinity of attainment of peak pressure. Typical pressure temperature profiles for hydroxypropylation reaction of kraft and steam explosion lignins are shown in Figures 3and 4. The reactions were terminated as soon as the pressure dropped below 100 psi.



Figure 3: Pressure Temperature Profiles for Hydroxypropylation of Kraft lignin.



Figure 4: Pressure Temperature Profiles for Hydroxypropylation of lotech Lignin.

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After cooling, the contents of the reactor were freed from tolylene and unreacted propylene oxide by vacuum evaporation. Products resulting from homopolymerization of propylene oxide were separated from hydroxypropyl lignins by n-hexane extraction of acetonitrile solution in a liquid-liquid extractor for a period of 24 hours.

#### 3.2 METHODS

#### 3.2.1 Material Characterization

#### Lignin Degradation by Permanagnate Oxidation

The utility of alkaline permanaganate as an effecient depolymerizing material for lignin has been discussed elsewhere.<sup>88-90</sup> Conventionally the method is applied in parallel to an authentic and cupric oxide depolymerized lignin preparation by DMSO4-methylation, oxidation by permanaganate and hydrogen peroxide and methylation by diazomethane. A revised procedure<sup>91</sup> was used in the reconstruction of structure.

#### Gas Chromatographic Analysis of Degradation Products

The methyl esters from permanganate oxidation are analysed by gas chromatography using pyromellitic acid as an internal standard. The conditions for the analysis are given below.

Column: 5 ft long glass column packed with 3% SP2100.

Nitrogen flow: 28 ml/min.

FID temperature: 300°C

Injector temperature: 280°C

Column temperature program: Initial 115°C

Final 250°C

rate of rise: 4°C/min.

#### Gel Permeation Chromatography of Hydroxypropylation Products

Molecular mass and molecular mass distributions of lignins were determined on а set of four µ spherogel columns based on styrene-divinyl benzene copolymer. Dimethyl formamide was used as solvent and 0.1 M concentration of lithium bromide was employed as The column calibrated dissociating electrolyte. set was with monodisperse polystyrene standards.

#### Vapor Pressure Osmometry

Number average molecular weights were determined with Knauer Vapor Pressure Osmometer. The instrument was operated at 90°C with dimethylformamide as solvent. For lignin samples, coumaran methyl ether was used as a standard for calibration. Concentrations ranged between 0.02 to 0.10 M.

#### Proton NMR of Lignins and Hydroxypropyl Derivatives

A sample of approximately 50 mg of lignin or hydroxypropyl lignin was acetylated overnight with an acetic anhydride and pyridine mixture, under nitrogen. The reaction mixture was then precipitated into ethyl ether, filtered and washed with ether. The sample was dried over phosphorous pentoxide and the spectrum of the sample was recorded from a deuterated chloroform or deuterated dimethyl sulfoxide solution.

#### FT:IR of Lignins and Hydroxypropyl Derivatives

Infrared spectra of lignins were recorded using potassium bromide pellets prepared using 1 mg lignin and 200 mg potassium bromide. Hydroxypropyl lignins were cast as thin films on sodium chloride plates in tetrahydrofuran solution for the spectral examination with Nicolet MX-1 Spectrometer.

#### Isocyanate Demand of Polyol

Weighed polyol was mixed with an excess of butyl isocyanate in methyl ethyl ketone and refluxed for two hours. The excess of butyl isocyanate remaining after the reaction was estimated by the butylamine titration method described below.

The refluxed mixture with excess butyl isocyanate was transferred in to 250-ml erlenmeyer flask fitted with stopper. 40 ml of 2 N solution of di-n butylamine in dry toluene was added and brought to reflux in 3 to 4 minutes. The boiling was allowed to continue till the reflux line reached the etched markings on the flask. The mixture was allowed to cool for a period of 20 minutes and titrated against standardized 1 N hydrochloric acid solution with bromophenol blue indicator. A blank was run on butylamine solution to determine its strength. Isocyanate equivalent and the percent NCO in the mixture was calculated as follows:

A = ml. of 1N HCl used for sample B = ml. of 1N HCl used for blank N = Normality of HCl used

I.E = 1000(sample weight)/{(B-A)(N)} % NCO = 4200/I.E.

#### Film Preparation

Polyurethane films were prepared from the two diisocyanates and the two hydroxypropyl lignins (HPLs) Polyols were dried by degassing under vacuum prior to use. The polyol component, the isocyanate, and the catalyst were thoroughly mixed in tetrahydrofuran (THF) solution and allowed to stay for 5 minutes; the formulation was then poured on glass plates coated with a thin layer of silicone oil L-520 (Union Carbide The Corporation). casting concentration of the polyurethane formulation was about 20.0 percent in all cases. Dibutyl tin dilaureate (T-9 Catalyst, Union Carbide Corportion, South Charleston, W.Va) was used as catalyst in concentrations amounting to 3.0% on solids. The resin was allowed to stand for about 15 minutes, at room temperature in a hood to evaporate part of the solvent and set in the form of a uniform film. Subsequent cure was carried out in an air circulated oven for three hours at 105°C. The films were stored in a desiccator for at least one week before testing.

#### 3.2.2 Product Analysis and Testing

#### Differential Scanning Calorimetry (DSC)

DSC was performed using a Perkin Elmer model DSC 4 equipped with scanning auto zero accessory. Heating rate was 10°C/min and sensitivity

2 mcal/s. Dry Nitrogen was used as purge gas. Samples were cut directly from vacuum dried solvent cast films to a weight of 18-22 mg. The glass transition temperatures were determined by the change in heat capacity of one half of its maximum value as suggested by Perkin-Elmer Corporation.

#### Stress-Strain Testing

Uniaxial stress-strain and ultimate property measurments were made using a standard Instron testing machine employing a cross-head speed of 1 mm/min. Samples were cut with a die in a dog bone shape, from solvent cast films. Tensile characteristics were calculated on the basis of initial dimensions (gage length 10 mm and width 2.8 mm.)

#### Swelling

Polyurethane films were swollen to equilibrium (120 hrs) in dimethylformamide. The increase in weight due to swelling was expressed on unswollen weight.

#### Small Angle X-ray Scattering

A standard Kratky small angle X-ray camera was used for the SAXS experiments. The X-ray source was a Siemens AG Cu 40/2 tube, operated at 40kV and 20MA. The generator was a General Electric XRD-6 unit, and cooling water at  $65\pm0.5^{\circ}$ F was circulated by a Haskriers cooler. Cu K $\alpha$  monochromatic beam ( $\lambda$ =1.542 A) was obtained by Ni foil filtering. The counting of the X-ray intensity was performed by a Siemens sealed proportional gas detector, in conjunction with a pulse height analyser. The camera motor was controlled by a PDP/8a computer which also served for data acquisition.

#### Dynamic Mechanical Analysis

Dynamic Mechanial Analysis was performed using a Rheovibron DDV-II viscoelastometer (Toyo Measuring Instruments Co., Ltd). Sample thickness ranged from 0.1-0.15 mm. Samples were initially quenched from room temperature to approximately -125°C and then heated at a rate of 1-2°C/min. Icing of the specimens at low temperature was avoided by sweeping dry nitrogen through the chamber. Data were taken at approximately 2°C intervals.

#### Scanning Electron Microscopy

Scanning electron micrographs of the films were taken with an advanced Metals Research Model 900 instrument. The samples were coated with gold-palladium alloy prior to the scans.

#### Chapter IV

#### CHARACTERIZATION OF LIGNINS AND HYDROXYPROPYL LIGNINS

#### 4.1 CHEMICAL ANALYSIS

The general concept of interpreting primary analytical information gained with an isolated lignin preparation has been discussed elsewhere. 10 Analytical data pertaining to elemental composition, methoxyls, total hydroxyls, carbonyls and impurities in the form of ash and hydrolyzable sugars, and gas and gel permeation chromatography data obtained with the permanganate oxidation mixtures is converted by the analysis program to define the phenylpropane substructure of lignin. The simulation techniques described elsewhere<sup>5</sup>-<sup>8</sup> are then used to model lignin structure which is analyzed in reversed analysis program to produce degradative data to match with the experimental data. The combination of these simulation programs thus allows to reconstruct the original structure of the isolated lignin preparation.

Proton magnetic resonance spectra of the acetylated derivatives of kraft and lotech lignins and their hydroxypropyl derivatives (HPLs) are given in the appendix. The results of chemical analysis are given in Table 1. The data were interpreted with simulation techniques and the results are given in Table 2. Kraft lignin based on pine has a lower
syringyl content than lotech lignin based on aspen. The para hydroxy phenylpropane units are present to the same extent. The presence of a higher number of phenolic hydroxyls in kraft lignin is due to an extensive cleavage of alkyl-aryl ether bonds during pulping. The presence of a higher phenolic hydroxyl content in lotech lignin as compared to milled wood lignin has been reported<sup>#6</sup> and is beleved to be a result of partial hydrolytic cleavage of the ether bonds in the explosion process. The average molecular weight of kraft lignin is considerably higher than lotech lignin and the values match with those reported in the literature. The low solubility characteristics for kraft lignin have been observed and attributable to network character, and internal hydrogen bonding.

The proton NMR spectra of the two HPLs were interpreted as per the procedure discussed elsewhere.<sup>34</sup> The distribution of protons for kraft HPL was found to be 16.8% in the aliphatic acetoxy range (range 5) and 24.0% in the range of methyl protons (range 6). The distribution for lotech HPL in these ranges were 19.8 and 22.5% respectively. Accordingly, the hydroxyl content for kraft and lotech HPL were calculated to be 4.3 and 9.3% respectively, on weight basis. Conversion of all the reactive groups (primary and secondary hydroxyls and carboxyls) in lignin to secondary hydroxyls in HPLs is expected to retain the equivalence of functionalities on hydroxypropylation. The unit weight (average phenylpropane unit) of kraft lignin is 346.2 by SIMREL<sup>5-10</sup> and the expected value of hydroxyl content is 3.81%. The

# Elemental Composition and Functionality

Property	Kraft Lignin	Iotech Lignin			
I. Elemental analysis (%)					
C H S	64.33 5.88 2.10	61.90 5.34 0.00			
II. Functionality (%)					
OCH3 Total OH Phenolic OH Carbonyl	13.70 11.86 5.52 0.93	18.23 9.59 4.25			
III. Carbohydrates (%)					
Total Hexoses Pentoses	0.73 0.51 0.22	0.60 0.31 0.29			
IV. Molecular Weight (g /mol)					
M <sub>n</sub> (GPC) M <sub>w</sub> (GPC) M <sub>n</sub> (∨PO)	1278 4280 1446	558 1928			

# Composition of Average Phenylpropane Unit

Property	Kraft Lignin	lotech Lignin	
I. Composition of average Phenylpropane unit			
Total H Aromatic H Total OH Phenolic OH OCH <sub>3</sub> SH Unit weight	8.10 2.51 1.32 0.66 0.81 0.12 181.6	7.00 2.10 1.14 0.49 1.13 0.00 197.9	
11. Approximate linkage distribution per 100 C <sub>g</sub> units			
AI-5 AI-2/6 1/5-5,4-0-5 AI-0-4	10-15 2-4 40-45 30-35	2-5 6-8 17-22 28-32	
III. C <sub>9</sub> Unit Type			
Guaiacyl Syringyl p-hydroxy	0.80 0.01 0.19	0.52 0.31 0.17	

Note: Total H does not include protons in  $OCH_3$ ,  $OC_3H_6$  and SH Al - Aliphatic carbon

demand as determined with butyl isocyanate titration isocvanate indicated 3.083 meg/g of isocyanate reactive functionality; assuming only hydroxyls in HPLs as reactive groups, the hydroxyl content amounts to 5.24%. Thus for kraft HPL the values are close to that expected, assuming unimolar addition of propylene oxide moities to reactive hydroxyls. Slight discrepancy between the observed and the expected values can result from water and homooligomer impurities or the reaction of propylene oxide with other reactive groups. Large excess of hydroxyls generated during hydroxypropylation of lotech lignin however, is possibly due to cleavage of residual alkyl-aryl ether bonds in the alkaline conditions of hydroxypropylation. The support for this comes from the fact that lotech lignin has more cleavable ethers due to a milder form of isolation. For the purpose of calculation of the molar ratios in the polyurethane formulation however, the values from NMR are taken as representative.

## 4.2 SPECTRAL ANALYSIS

The FTIR spectra of the two lignins and their hydroxypropyl derivatives are given in the appendix. Certain changes in absorptions on hydroxypropylation can be noted, mainly in the region of hydroxylic and carboxylic absorptions.

Hydroxyl Groups.

The O-H stretching frequencies of aliphatic hydroxyls in  $3500 \text{ cm}^{-1}$ region occur at somewhat higher range than phenolic hydroxyls. The frequencies for the range, show a clear shift on hydroxypropylation. The bands in the region 1376 -1325 and 1220 -1170 cm<sup>-1</sup> are also of interest. There exists a controversy on the structural feature in lignin gives rise to these bands.<sup>92</sup> Whereas 1370 cm-<sup>1</sup> band is which diminished by deuteration,<sup>93</sup> pointing to the hydroxylic character, it is retained on diazomethane methylation pointing to the assignment to C-H deformation.<sup>94</sup> The spectral studies on hydroxypropylated lignins, both in case of kraft and lotech, showed the band at 1370 cm<sup>-1</sup> is unaffected on hydroxypropylation whereas the band at  $1220 - 1170 \text{ cm}^{-1}$  disappears. This indicates that the 1376 -1325 cm-1 and 1220 -1170 cm-1 absorptions possibly originate from and phenolic hydroxyls, respectively. There is a simultaneous appearance or intensification of band at 1240- 1230 cm<sup>-1</sup>, attributable to ether links. The changes in the spectral features are shown in Figure 5. Lignin model compounds with secondary hydroxyl groups show an absorption around 1076 cm-1. Diagnosis of secondary alcohols from this band is complicated by a strong absorption at 1125 -1085 cm<sup>-1</sup> and a weak band at 1065 -1025 cm<sup>-1</sup>, originating from C-O-C deformation of aliphatic ethers.<sup>92</sup> The etherification of model compounds results in a decrease of relatively strong absorption band at  $1075 \text{ cm}^{-1}$ and appearance of bands at 1065, 1090 and 1115 cm<sup>-1</sup>. The examination of lignins and the hydroxypropyl derivatives shows appearance of the 1090 cm<sup>-1</sup> band assignable to C-O deformation in secondary alcohols and aliphatic ethers. In case of lotech HPL however, the band seems to be broadened by the one at 1127 cm<sup>-1</sup> as shown in Figure 6. The stronger absorption at 1111 cm<sup>-1</sup> seems to indicate that lotech lignin has higher polyether content, compared to Kraft lignin. The simultaneous diminishing of the band in the region of 1045 -1020 cm<sup>-1</sup> assignable to primary alcohols is evident by the comparison of the spectra of lignins and their hydroxypropyl derivatives.

On the basis of these observations it is reasonable to conclude that most of the phenolic hydroxyls are etherified on hydroxypropylation. It should be noted that using appropriate lignin like model compounds, Ishikawa et al.<sup>95</sup> have demonstrated that phenolic hydroxyls react quantitatively with ethylene oxide if the side chains do not contain carbonyl groups or unsaturated moities.

### Carboxyl Groups

Some investigators in the past have assigned the absorption at 1720 cm<sup>-1</sup> in hardwood lignins to aromatic ester groups, <sup>96</sup>, <sup>97</sup> but this value is clearly too high to have originated from this source. <sup>92</sup> Assignment of aliphatic carboxyl groups to 1720 cm<sup>-1</sup> wavelength is much preferable. <sup>98</sup> Studies on methanol extracted lotech lignin from aspen<sup>86</sup> indicated the assignment of these bands to unconjugated carbonyls or esters but the <sup>13</sup>C NMR failed to reveal any signal around 200 ppm attributable to such groups. Studies by Conrat et al.<sup>99</sup> showed that in alkaline medium, the esterification of the carboxyl groups is a predominant reaction. The FT-IR spectra of lignins and their hydroxypropyl







Figure 6: FT-IR Spectrum in the Range 1400-800 cm-1

derivatives as in Figure 7. show that the bands in the region of 1720  $cm^{-1}$  in lignins are shifted to 1695-1650  $cm^{-1}$  on hydroxypropylation. This supports the assignment of the 1720  $cm^{-1}$  to carboxyl groups in lignin and the clear shift to the ester stretch frequency indicates the conversion of carboxyls almost completely to ester groups on hydroxypropylation.

It has been reported<sup>100</sup> that a simple relationship does not exist between the number of the methyl groups and the intensity of the absorption bands at 1470 -1460 cm<sup>-1</sup> which result from the asymmetric bending of methyl groups. The examination of spectra in the qualitative sense however, shows that the band increases in intensity and in case of lotech HPL even surpasses the intensity of the band at 1515 cm<sup>-1</sup>, indicating the addition of large number of propoxy units.

### 4.3 THERMAL ANALYSIS

The DSC scans of lignins and the corresponding HPLs is shown in figure 8. A rapid drop of glass transition temperature in both cases is observed. The magnitude of the drop is approximately same, and steam explosion lignin and the HPL have considerably lower glass transition temperature than kraft lignin and HPL.

The thermal behavior of lignin has been investigated by several workers in recent years.<sup>101-110</sup> However these have been limited to such analytical techniques employing the material in the powder form,



Figure 7: FT-IR Spectrum in the Range 2000-1400 cm<sup>-1</sup>



Figure 8: DSC Thermograms of Lignins and HPLs.

as it is difficult to prepare a coherent and void free solid from lignin, and usual polymer characterization procedures such as viscoelastic measurments can not be used.

In the study of spruce periodate and dioxane lignins, Ramiah and Goring<sup>103</sup> observed two types of transitions ( $T_1$  and  $T_2$ ) in the range of 25-31°C and 80-108°C respectively. It was inferred that  $T_1$  was attribuatable to weak hydrogen bonds resulting from the interaction of hydroxyl groups and  $T_2$  originated from motions of restricted chain segments. Hatakeyama et al.<sup>104</sup>-<sup>110</sup> investigated molecular motions in several softwood lignins by infrared spectrometry and glass transitions were ascribed to motion of aromatic rings. Investigating molecular motions in lignins by broad line nuclear magnetic resonance methods from -153°to 197°C the authors reported several transitions identifiable as hindered rotation of methoxyl groups, hindered motions of side chains, breakage of hydrogen bonds and glass transitions.

On the basis of the investigations carried out, it is evident that the glass transition temperature of a lignin sample is affected by molecular weight and its chemical history. Thermal transitions in lignin have been seen to be largely controlled by internal bonding. The effect of chemical modification is interpreted as blocking or eliminating various oxygen containing functional groups. Thus  $T_g$  of kraft lignin was found to decrease on acetylation, methylation with dimethyl sulfate, and methylation with diazomethane.<sup>1</sup> Hydroxypropylation is also seen to have a similar effect.

#### Chapter V

## STRUCTURE-PROPERTY RELATIONSHIPS IN LIGNIN BASED POLYURETHANES

### 5.1 SYNTHESIS

The synthesis of thermosetting polymer films from components which have the tendency to gel before the completion of the reaction is best accomplished by solution casting. Formation of the film before the onset of gelation is necessary and removal of the solvent and completion of the cure at elevated temperature can be carried out subsequently. However, this leads to a certain probability that some of the isocyanate is lost in the process and creates a difference between the composition of the formulation and the one existing in the film. Also, use of higher catalyst content compared to conventional processes, and excess amount of diisocyanate become necessary to achieve complete reaction.

It is interesting to compare one related study by Minoura et al.<sup>66</sup> on polybutadiene glycol (Polybd, R45-HT) with a functionality in excess of two. The polyurethanes based on this glycol were synthesized in bulk with stoichiometric quantities of diisocyanates. The authors emphasize the complications arising due to gelation in the elastomer preparation and the necessity of quick casting. Also, it was observed that the benzene extractables ranged form 2.0 percent in the HDI based elastomers to 20.5 percent those based on HDI. The authors used the

compositions of the formulations as representative of film compositions, but it is questionable to ignore the possibility of losses in the process particularly with volatile diisocyanates like HDI and TDI. It should be noted that with solution casting procedure, similar to synthesis of lignin based polyurethanes, efforts to prepare polyurethane elastomer from polybutadiene glycol (Polybd R45-HT, ARCO Chemical Comapany), in solution with stoichiometric quantities of diisocyanates were not successful. The glycol remained largely unreacted when stoichiometric quantities of HDI or TDI were used, indicating it is difficult to adhere to exact stoichiometry when films have to be cast before the completion of reaction, to prevent gelling in solution. Thus employment of excess quantities of diisocyanate in lignin based polyurethanes has to be viewed as a restraint imposed due to the modification of the solution casting procedure, to avoid gelling before the formation of film.

Table 3 summarises the compositions of formulations used to synthesize the films. The films are designated as KH and KT types on whether they were prepared with HDI or TDI, depending respectively and hydroxypropylated kraft lignin; similarly IH and IT series are based on steam explosion lignin (lotech Lignin) and HDI and Synthesis of polyurethane film can be very TDI, respectively. sensitive to either the type lignin or the range of NCO/OH ratio. Between the two HPLs, the sensitivity of the hydroxypropylated steam explosion lignin to variation of isocyanate content was found to be a controlling factor. The NCO/OH ratio of less than 1.5 in case of HDI

and 1.4 in case of TDI resulted in a very brittle material unsuitable for mechanical testing. No comparable problems were observed in case of hydroxypropylated kraft lignin. The only current explanation for this observation, is the low molecular weight of lotech lignin and a minimum level of bond requirement for the synthesis of films of sufficient mechanical strength. In these lignin derived polyurethanes prepared with excess NCO/OH ratio, three types of bonds as shown in Figure 9 can produce crosslinks. Biuret links can originate from any residual moisture content. The allophanate links resulting from the reaction of excess diisocyanate with urethane groups are likely to be more prevalent.<sup>111</sup> Thus increase in the NCO/OH ratio results in the formation of higher number of crosslinks which produce material of sufficient strength, but at the same time result in higher rigidity characteristics.

## 5.2 THERMAL AND SWELLING BEHAVIOR.

The DSC thermograms of the polyurethanes are shown in Figure 10-13. It is observed that the glass transition temperatures of polyurethanes are higher than the glass transition temperatures of the HPLs but generally below those of lignins. An increase of glass transition temperature with increase in the NCO/OH ratio is observed in all four series. With the highest ratio of NCO/OH (4.56) the T<sub>g</sub> of the polyurethane is even higher than that of kraft lignin.

Compositions of Hydroxypropyl Lignin Based Polyurethanes.

Designation	HPL Type	Component Wt. Fraction, %	lsocyanate Wt. Fraction, %	NCO/OH Ratio
HDI Series KH-1 KH-2 KH-3 KH-4 KH-5	Kraft	50.0 55.5 62.5 71.5 83.3	50.0 44.5 37.5 28.5 16.7	4.7 3.8 2.8 1.9 0.9
IH-1 IH-2 IH-3	loteċh	50.0 54.1 57.0	50.0 45.9 43.0	2.2 1.9 1.6
TDI Series KT-1 KT-2 KT-3 KT-4 KT-5 KT-6 KT-7	Kraft	50.0 55.5 62.5 71.5 83.3 76.9 87.0	50.0 44.5 37.5 28.5 16.7 23.1 13.0	4.6 3.7 2.7 1.8 0.9 1.4 0.7
IT-1 IT-2 IT-3 IT-4 IT-5	lotech	42.9 46.2 50.0 54.5 60.0	57.1 53.8 50.0 45.5 40.0	2.8 2.5 2.1 1.8 1.4



Figure 9: Principal Bond Formations Producing Crosslinks in Thermosetting Kraft Polyurethanes.



Figure 10: DSC Thermograms of KH- Series Polyurethanes.





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Figure 12: DSC Thermograms of IH- Series Polyurethanes.



Figure 13: DSC Thermograms of IT- Series Polyurethanes.

Glass transition temperatures of the polyurethanes are given in Between the two isocyanates selected for the study, TDI Table 4. based polyurethanes have  $T_{\alpha}s$  higher than that of HDI for the same NCO/OH ratio as can be noted from Figure 14. Smith et al.<sup>112</sup> compared HDI and TDI polyurethanes elastomers based on poly (oxypropylene) glycols and observed higher glass transition temperatures for the latter. Similar results were obtained by Guise et al.<sup>71</sup> for poly- $\varepsilon$ -caprolactone diol based polyurethanes. In lignin based polyurethanes, it is also observed that the  $T_{\alpha}$  of TDI based polyurethanes is much higher than that of HDI based polyurethanes irrespective of the composition. In addition,  $\mathsf{T}_{\alpha}$  rises more steeply with NCO/OH ratio.

It is noted that the glass transition temperature of the polyurethane begins to drop at very high isocyanate content in case of HDI. While it is possible that the crosslink density is still increasing at this point the probable reason for the drop in the  $T_g$  is that the segmental contribution by HDI through the hexamethylene 'soft segments' also increases proportionate to crosslinks. Figure 15 shows the swelling tendencies of the HDI polyurethanes in dimethylformamide. It is observed that there is no apparent decrease in swelling with NCO/OH ratio greater than 2.8. These two observations thus suggest that in case of HDI, the network crosslink density remains constant or even decreases with NCO/OH ratio; with TDI however, the  $T_g$  increases almost linearly until about the ratio of 3.6 at which it reaches a



Figure 14: Glass Transition Temperatures of HDI and TDI Based Kraft Polyurethanes in Relation to Composition.

constant value. It should thus be expected that the contribution to the network flexibility, possible in case of HDI, is absent in TDI. In the latter case the only effect of increasing the NCO/OH ratio is the synthesis of more rigid network structure.

Hydroxypropylated steam explosion lignin based polyurethanes were studied in a smaller range of NCO/OH ratio variations.  $T_gs$  of these polyurethanes are lower than those of kraft polyurethanes at the same molar isocyanate to hydroxyl ratio. The  $T_g$  of hydroxypropylated steam explosion lignin is lower than the kraft equivalent, and hence the result is not unexpected. However it is interesting to note that the IT polyurethanes have,  $T_gs$  very close to those of the KT polyurethanes at the same NCO/OH ratio.

### 5.3 STRESS-STRAIN BEHAVIOR.

The four thermosetting polyurethanes series based on two lignins and two diisocyanates, were examined for the effect of network crosslink density on mechanical properties. Table 4 summarises the ultimate properties of the polyurethanes, and it is seen that the properties are in general characterisitic of rigid materials.

It is observed that tensile strengths have hardly any sensitivity to NCO/OH ratio as can be seen for the kraft lignin polyurethanes (Figure 16). Average values of Young's modulus for the four series of



Figure 15: Swelling Tendencies of HDI Based Kraft Polyurethanes in Relation to Composition.

Properties of Hydroxypropyl Lignin Based Polyurethanes

Sample	NCO/OH	Young' <b>s</b>	Ultimate	Ultimate	Та
	Ratio	Modulus MPa	Stress MPa	Strain %	Č.
KH-1	4.7	1398±127	75.5	14.9	114
KH-2	3.8	1283±95	79.2	12.7	126
KH-3	2.8	1327±31	79.6	16.5	118
KH-4	1.9	1671±51	73.5	6.8	105
KH-5	0.9	1591±92	14.8	1.2	96
KT-3	2.7	1509±400	54.4	7.0	189
KT-4	1.8	2076±318	48.5	6.0	158
KT-6	1.4	1874±168	49.2	3.8	128
KT-5	0.9	1975±298	57.2	5.1	136
IH-1	2.2	1698±168	80.5	12.1	94
IH-2	1.9	1597±78	85.7	13.4	84
IH-3	1.6	1792±140	70.5	7.0	74
IT-1	2.8	1915±102	86.4	10.0	192
IT-2	2.5	2268±355	86.2	7.4	174
IT-3	2.1	2387±164	95.0	7.5	165
IT-4	1.8	2018±127	80.9	7.8	146
IT-5	1.1	2086±52	91.6	8.4	157

polyurethanes are shown in Figure 17. The moduli of the polyurethanes are comparable to the value of 2000 MPa for pine kraft lignin by torsion braid analysis.<sup>1</sup> With TDI as diisocyanate, the polyurethanes have higher modulus than with HDI which is expected because of introduction of rigid aromatic rings in the system. In the case of TDI polyurethanes (TDI -series) concentration of isocyanate has one influence in common with the HDI polyurethanes (KH-series): while increasing NCO/OH ratio is expected to increase the frequency of the bonding of the adjacent lignin structures, it is not expected to increase the 'soft segment' content, as discussed with reference to the DSC data. It is to be noted that while the highest NCO/OH ratio resulted in a strong polyurethane in KH-series, the corresponding polyurethane in KT-series produced a very brittle material. For this reason KT-1 and KT-2 with NCO/OH ratio of 4.56 and 3.66 could not be studied for the stress-strain behavior; nor could KT-7 with the ratio of 0.68, but the posssible reason in this case is the incomplete utilization of the hydroxyls.

The relative insensitivity of the Young's moduli in these polyurethanes to NCO/OH ratio is notable. Increasing NCO/OH ratio, should increase the frequency of allophanate crosslinks and should reduce the average molecular weight between crosslinks  $(M_c)$ . The insensitivity of modulus to composition can best be understood in terms of behavior of glassy network systems. In the study of crosslink density distribution on the engineering behavior of epoxies Misra et



Figure 16: Tensile Strengths of KH- and KT-Series Polyurethanes in Relation to Composition.



Figure 17: Average Values of Modulus for Lignin Based Polyurethanes Based on Two Lignins.

al.<sup>76</sup> have studied the effect of  $M_c$  (average molecular weight distribution between cross links) on the modulus behavior. Although the glass transition temerature exhibited the expected decrease with increasing  $M_c$ , the modulus remained fairly constant and independent. The observation was attributed to the glassy nature of the system at room temperature at which the long range segmental motion of the chains is frozen and is not manifest in the tensile characteristics. However, the authors note that the effect of  $M_c$  is not observable even above the  $T_g$  of the system as deduced from the creep experiments. The general explanation of this behavior from bisphenol-A based epoxies is that the bulky groups restrict the motion of the main chains.

Polyurethanes based on steam explosion lignin have a higher range of modulus compared to those based on kraft lignin. Increase in modulus with NCO/OH ratio is also steeper in comparison to kraft polyurethanes. Tensile strength values are also significantly higher and this must be interpreted both with reference to the functionality and the molecular weight of the original oligomers and the inherent structural differences because of the lignin type. lotech lignin has a very low molecular weight corresponding to an average of 2-3 phenylpropane units as compared to kraft lignin which has 6-7 units. The hydroxyl content of the hydroxypropylated steam explosion lignin is about twice that of the hydroxypropylated kraft lignin. Because lotech lignin lignin is based on hardwood (Aspen) it is also richer in syringyl structures. Higher hydroxyl content can be considered responsible for the increased internal bond strength and consequently higher stress levels at break.

The strain values at break are plotted in Figure 18 against NCO/OH ratio. There is no distinct trend observable in KTseries polvurethanes; KH- series however shows increase in maximum extensibility with NCO/OH ratio. This is a rather surprising result, because increasing crosslink density is expected to produce the opposite trend. It is probable that other factors contribute to this observation. Internal bond strength is one explanation as the ultimate properties are influenced more by chain breakage than slippage in these highly condensed polyurethanes. The increasing isocyanate content serves to bridge lignin moities with more urethane bonds and if the failure is dependent on the bonds produced in polyurethane synthesis, then the fracture may not occur till much higher elongations. If this explanation is valid then the KH-4 having higher stress at break as compared to KH-5 can be understood as a result of complete consumption of the hydroxyls in the former; and higher elongation at break in KH-1 as compared to KH-4 as a result of influence of allophante crosslinks and larger concentration of hexamethylene 'soft segments'. The swelling data showing hardly any increase in crosslink density at very high NCO/OH ratios, and a plateau or even a decrease in glass transition temperature can be considered as supporting observations for this explanation.



Figure 18: Ultimate Strain Values of Kraft Polyurethanes in Relation to Composition.

#### Chapter VI

## NETWORK MODIFICATION OF KRAFT POLYURETHANES WITH POLYETHYLENE GLYCOLS

## 6.1 SYNTHESIS

Table 5 summarises the compositions of formulations used in the films. Terminology of the polyurethanes is based on the diisocyanates used for the synthesis (KEH- series for HDI and KET- series for TDI), as well as the molecular weight of polyethylene glycol. In all the individual members of the series the weight contribution by isocyanate kept constant amounting to 28.6% of the formulation. Thus was depending on the molecular weight of the glycol the actual NCO/OH ratio would change. The ratio drops from KEH-400-1 to KEH-400-6, whereas it increases from KEH-4000-1 to KEH-4000-6. The relevance of control of molar ratio becomes rather superfluous in these polyurethanes, as achievment of complete reaction necessitates the quantities of the diisocyanate. employment of excess Choice of the compositions was isocvanate content of 28.6% in based the observation that all polyurethanes were homogeneous regardless of molecular weight of the soft segment glycol or its concentration. Higher isocyanate use in the formulation resulted in brittle materials even though the consumption of hydroxyls was readily completed and the

films cured well. Reduction of isocyanate content generally resulted in incompletely reacted and inhomogeneous films.

### 6.2 THERMAL BEHAVIOR

The DSC thermograms of TDI based kraft polyurethanes with polyethylene glycols as components are shown in Figure 19-22. The glass transition temperatures of the polyurethanes are summarised in Table 6. The data refer to lignin phase transition transitions originating from polyethylene glycol component were not detectable. The occurence of the enthalpy relaxation effects made it necessary to consider the second DSC scan (which was always reproducible) for the determination of  $T_g$ . The polyurethanes show a consistent drop in the glass transition with increasing amount of glycol. It is also observed that increase in the molecular weight of the soft segment is accompanied by increase in the glass transition temperature.

The absence of detectable glass transition attributable to polyethylene glycol phase suggest the these network polyurethanes have both the polyol components in well mixed state. The rapid drop in glass transition of lignin phase also points to the same conclusion. On the other hand, the inability to detect polyethylene glycol transition may be the result of both, the low weight contribution of polyethylene glycols and the general observation that phase separation tendencies are diminished in thermosets.

Compositions of Kraft HPL - Polyethylene Glycol Urethane Systems

Designation	Hydroxy		Isocyanate	NCO/OH Ratio			
	Weight	nent %	Component Weight %	at 400	EG Mo 600	1000	4000
	HPL	EG					
HDI- Series							
KEH-MW-1	71.4	0.0	28.6	1.89	1.89	1.89	1.89
KEH-MW-2	67.9	3.5	28.6	1.80	1.86	1.91	1.97
KEH-MW-3	64.3	7.1	28.6	1.73	1.83	1.93	2.06
KEH-MW-4	60.7	10.7	28.6	1.65	1.80	1.95	2.15
KEH-MW-5	57.1	14.3	28.6	1.58	1.78	1.97	2.25
KEH-MW-6	53.6	17.8	28.6	1.52	1.75	1.99	2.36
TDI- Series							
KET-MW-1	71.4	0.0	28.6	1.83	1.83	1.83	1.83
KET-MW-2	67.9	3.5	28.6	1.74	1.80	1.85	1.90
KET-MW-3	64.3	7.1	28.6	1.66	1.77	1.87	1.99
KET-MW-4	60.7	10.7	28.6	1.59	1.74	1.89	2.08
KET-MW-5	57.1	14.3	28.6	1.53	1.72	1.91	2.18
KET-MW-6	53.6	17.8	28.6	1.47	1.69	1.93	2.28

Note: Individual sample designations have numbers corresponding to molecular weight of Glycol in place of MW.

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Figure 19: DSC Thermograms of KET-400- Series Polyurethanes.


Figure 20: DSC Thermograms of KET-600- Series Polyurethanes.



Figure 21: DSC Thermograms of KET-1000- Series Polyurethanes.



Figure 22: DSC Thermograms of KET-4000- Series Polyurethanes.

Glass Transitior	n Temperatu Polyethyl	res of HDI I ene Glycol S	Based Kraft P oft Segments	olyurethanes	wit
Glycol Wt.%	E.G400	E.G600	E.G1000	E.G4000	
HDI Series					
0.0	105	105	105	105	
3.5	96	108	99	110	
7.1	87	94	88	96	
10.7	66	66	67	84	
14.3	56	56	65	76	
17.8	38	96	44	63	
TDI Series					
0.0	158	158	158	158	
3.5	120	148	157	131	
7.1	119	130	143	155	
10.7	86	128	131	120	
14.3	79	97	110	108	
17.8	70	41	95	95	

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The interpretation of the observations on the trends in the glass transition temperature with glycol molecular weight is complicated because of the difficulty in decoupling the effects originating from variation of molecular weight of glycol and the variation in crosslink density brought about by changing NCO/OH ratio. Comparison at equivalent number of chain introduction is also difficult as this can bring two very different systems for comparison; thus for kraft polyurethanes with polyethylene glycols, comparison under this condition would necessitate a ten times as high a weight content for a ten-fold increase in molecular weight.

However, trends observed in the shifts of glass transition related to the glycol molecular weight can be temperatures as rationalised. Two contributing factors can be considered. For the same weight contribution of the glycol, the number of chains introduced in the network decrease with the molecular weight. Secondly, as the stoichiometric isocyanate requirement of the glycol also decreases with molecular weight, use of constant weight contribution of diisocyanate result in increased crosslink density. These factors, should in conjunction would tend to increase the glass transition temperature of the However, it is to be noted that increase in molecular lignin phase. weight of glycol is expected to decrease glass transition temperature (of linear strands) in a network. Any effect of polyethylene glycol molecular weight on the glass transition of lignin phase is either masked or not significant in comparison to effects of number of chain segments or crosslink density.

#### 6.3 SWELLING

Swelling tendencies of HDI based kraft polyurethanes are plotted NCO/OH ratio in 23. The swelling increases against Figure proportionate to glycol content in polyurethanes modified with polyethylene glycols of molecular weight 400, 600 and 1000. For molecular weight of 4000 however, the swelling behavior is similar only at low glycol contents. As the glycol content is increased, the swelling begins to decrease and, in the range of glycol content examined, finally levels off to a constant value.

It is to be noted that eventhough the swelling properties of series with polyethylene glycols of molecular weight 400, 600 and 1000 are similar, for the last series (1000), NCO/OH ratio increases with glycol content as opposed to the first two. The observation on swelling indicates that crosslink density effects brought in by increased NCO/OH ratio, do not play as important a role as the increase in average  $M_c$  due to glycol incorporation. Only at a higher range of crosslink density, the effects become apparent, as seen for polyurethanes with polyethylene glycol of molecular weight 4000. In this case the initial increase in swelling with glycol content (and increasing NCO/OH ratio) is similar to polyurethanes with glycol molecular weight 1000. However, with higher glycol content the swelling decreases, suggesting that



Figure 23: Swelling Behavior of HDI Based Polyurethanes.

crosslink density becomes a controlling factor. It is noted that near constancy in the extent of swelling at high NCO/OH ratios was also observed in polyurethanes without glycols, and similar to the conclusion arrived before, it is possible that the effect of increased crosslinks is offset by increase in average  $M_c$ .

#### 6.4 STRESS-STRAIN BEHAVIOR

The ultimate strength properties of kraft polyurethanes with soft segment incorporation are given in Tables 7 and 8. Figures 24-27 show typical tensile behavior of HDI based polyurethanes. Glycol content clearly has a more significant effect in comparsion to molecular weight. It is also evident that even a minor percentage of polyethylene glycol has significant influence on the tensile behavior of the materials. The modulus is also seen to decrease with increasing weight fraction of the glycol. This is clearly observed in case of HDI based polyurethanes.

TDI based polyurethanes in general exhibit the effect of polyethylene glycols to a lesser degree; with PEG 400 changes are hardly observable, and the decrease is observed only at high weight fraction for PEG 600. Moduli are constant over the tested range of composition for PEG 1000. However there is a clear distinction for polyurethane films prepared with incorporation of polyethylene glycol of molecular weight 4000; whereas the trend in modulus of HDI polyurethanes is similar to other glycols, the modulus in TDI based polyurethanes increases with glycol content after an initial decline.

It is also interesting to note that some of the polyurethanes show yield properties. This is generally observed with HDI polyurethanes; TDI polyurethanes, by contrast, do not exhibit this behavior at either extremes (PEG 400 and PEG 4000). Also, occurence of yield point is seen to shift to higher glycol contents with molecular weight, except for PEG 4000. Yield stress and tensile strength both show an expected decrease with glycol content.

In these thermosetting polyurethanes, compositional changes seem to have a greater influence on strain at break, than on modulus or ultimate strength. Similar to observations on other properties, TDI polyurethanes hardly show any changes in ultimate strain values. Among HDI polyurethanes the increase in maximum extensibility is up to five times that of unmodified kraft polyurethane. The effect of glycol content on this property diminishes with increasing molecular weight at any particular weight contribution.

The sensitivity of HDI as opposed to TDI polyurethanes is primarily ascribable to the aromatic nature of the latter which masks the structural changes observable through the mechanical properties. The observed upward trend in modulus with constant weight contribution, and increasing molecular weight of the glycols is similar to the observations on glass transition temperatures and again, is interpreted as a function of actual number of chains introduced and crosslink density changes accompanying molecular weight changes.

## Tensile Properties of HDI Based Kraft HPL - Polyethylene Glycol Polyurethanes

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Sample	Kraft HPL wt.%	Young s Modulus MPa	Yield Stress MPa	Yield Strain %	Ultimate Stress MPa	Ultimate Strain %
KEH-400-1 KEH-400-2 KEH-400-3 KEH-400-4 KEH-400-5 KEH-400-6	71.4 67.9 64.3 60.7 57.1 53.6	1671±51 1042±38 1062±67 1618±42 707±112 384±38	48.6 39.7 53.8 30.8 19.2	8.1 5.9 4.9 7.2 9.3	73.5 46.4 34.8 44.4 31.2 26.0	6.8 9.4 15.4 11.0 24.9 43.0
KEH-600-1 KEH-600-2 KEH-600-3 KEH-600-4 KEH-600-5 KEH-600-6	71.4 67.9 64.3 60.7 57.1 53.6	1671±51 1034±33 965±30 865±60 716±49 1377±88	47.3 40.2 31.9 52.9	7.0 7.1 6.8 5.4	73.5 47.1 46.7 39.2 33.4 47.3	6.8 7.3 8.0 10.0 26.5 10.6
KEH-1000-1 KEH-1000-2 KEH-1000-3 KEH-1000-4 KEH-1000-5 KEH-1000-6	71.4 67.9 64.3 60.7 57.1 53.6	1671±51 1221±59 1085±50 942±62 745±28 594±37	43.1 35.8 27.8	6.8 7.0 8.0	73.5 51.5 50.2 41.6 35.0 29.0	6.8 5.8 6.2 9.2 9.6 19.8
KEH-4000-1 KEH-4000-2 KEH-4000-3 KEH-4000-4 KEH-4000-5 KEH-4000-6	71.4 67.9 64.3 60.7 57.1 53.6	1671±51 1272±89 1153±50 962±75 801±52 592±21	48.2 45.7 39.7 33.1 28.3	5.9 6.2 6.5 6.9 7.9	73.5 47.3 44.3 39.1 33.4 29.5	6.8 9.2 10.4 11.0 10.1 13.0

Tensile Properties of TDI Based Kraft HPL - Polyethylene Glycol Polyurethanes

Sample	Kraft HPL wt.%	Young's Modulus MPa	Yield Stress MPa	Yield Strain %	Ultimate Stress MPa	Ultimate Strain %
KET-400-1 KET-400-3 KET-400-4 KET-400-5 KET-400-6	71.4 64.3 60.7 57.1 53.6	2076±318 1706±140 2438±97 1946±68 1834±115			48.5 37.8 69.2 56.1 46.9	6.0 2.9 4.8 6.0 4.0
KET-600-1 KET-600-2 KET-600-3 KET-600-4 KET-600-5 KET-600-6	71.4 67.9 64.3 60.7 57.1 53.6	2076±318 1459±157 1400±102 1409±108 1448±87 592±71	60.6 30.0	6.4 7.7	48.5 62.9 64.4 63.1 57.2 33.7	6.0 5.9 6.8 7.6 8.8 31.0
KET-1000- KET-1000-2 KET-1000-3 KET-1000-4 KET-1000-4 KET-1000-4	1 71.4   2 67.9   3 64.3   4 60.7   5 57.1   6 53.6	2076±318 1590±57 1485±83 1531±150 1423±21 1317±38	50.7	5.3	48.5 50.5 52.9 55.5 51.9 45.8	6.0 3.3 4.1 4.6 5.6 10.2
KET-4000- KET-4000- KET-4000- KET-4000- KET-4000- KET-4000- KET-4000-	1 71.4 2 67.9 3 64.3 4 60.7 5 57.1 6 53.6	2076±318 1508±115 1524±129 1459±158 1780±121 1931±110			48.5 60.9 61.3 59.6 66.0 63.1	6.0 5.3 5.2 5.2 5.1 4.7







Figure 25: Tensile Behavior of KEH-600- Series Polyurethanes.

80-KEH-1000-SERIES 70-60-50-STRESS, J (MPa) 40· 30-20-10 231 45 6 0·15 0.05 ٦ 0.10 0.20 STRAIN, «

Figure 26: Tensile Behavior of KEH-1000- Series Polyurethanes.





#### 6.5 DYNAMIC MECHANICAL ANALYSIS

The dynamic mechanical spectra of three polyurethanes are given in Figures 28-30. It is noted that KH-4, KEH-600-6 and KEH-4000-6 represent the polyurethanes synthesized with identical weight fractions of isocyanate in all cases, and identical soft segment fraction in the latter two cases. The values of transition temperatures as measured at the occurence of the maximum in the tand peak are 125, 142 and  $120^{\circ}$ C The magnitudes of the tan $\delta$  are different in all the three respectively. polyurethanes; the values for KH-4, KEH-600-6 and KEH-4000-6 are respectively 0.42, 0.66 and 0.35. The transition in the two polyurethanes with polyethylene glycol is also broader as compared to pure kraft polyurethane, and occurs at lower onset temperatures. The transition begins at about 95°C for KH-4 and at 55° for KEH-600-6. With increase in molecular weight to 4000 the transition begins at even lower temperature (20°C).

The relative magnitudes of  $\tan \delta$  maximum, for KH-4, KEH-600-6, and KEH-4000-6 indicate that the energy dissipating characteristics are increased by glycol incorporation, and, as has been found in the thermal and stress- strain behavior of these polyurethanes, the maximum effect is found with lowest crosslink density and largest number of chains.

The examination of the storage and the loss moduli reveal the thermosetting characteristics in these materials. Crosslinking is







Figure 29: Dynamic Mechanical Spectrum of Polyurethane KEH-600-6.



Figure 30: Dynamic Mechanical Spectrum of Polyurethane KEH-4000-6.

expected to stabilize the modulus after the rubbery plateau, and, with these lignin based materials happens at about 165°C in KH-4 and KEH-4000-6. KEH-600-6 on the other hand shows a continuing drop in the modulus until 200°C (end of temperature program). The moduli for KH-4, KEH-600-6 and KEH-4000-6 are 92, 34 and 53 MPa respectively at 165°C and with the increase in temperature to 190°C, decrease to 72, 18 and 46 MPa. It is noted that the value of 18 MPa for KEH-600-6 as storage modulus at 200°C is not stabilised value, characteristic of thermosets. The magnitude as well as the behavior of modulus over the temperature range represents a significant extent of thermoplasticity introduced into the system by glycol inclusion.

There is another important difference between pure and glycol modified polyurethanes. The storage and the loss moduli curves show a weaker transition from 50 to 75°C for KEH-600-6 and from 15-45°C for KEH-4000-6, and this is not present in KH-4. The cause for this transition at this time can not be attributed to any structural feature but it seems to originate from the glycol component. Lagasse,<sup>60</sup> in the study of crosslinked polyurethane elastomers, showed the existence of domain structure by small angle X-ray scattering and electron microscopy, even though the crystallinity in the samples was not detectable. Lunardon et al.<sup>113</sup> reported an additional weaker transition besides two expected hard and soft phase transitions, and ascribed it to a mixed phase of soft and hard segments. In view of the magnitude of the transition in these kraft polyurethanes, and the range at which

it occurs, it is difficult to suggest any degree or purity of domains in the microstructure.

#### 6.6 SMALL ANGLE X-RAY SCATTERING

Figure 31 shows the intensity of scattering as a function of scattering angle for KEH-600-6 and KEH-4000-6. These represent highest weight fraction of the two glycols examined. The conditions for microphase separation are favourable, in view of molecular weight and concentration of soft segments. The samples were 0.55 mm thick in both cases and were prepared by stacking films to give a uniform thickness.

It is clear from the figure, the overall intensity of scattering is same at high angles. However, at smaller angles the intensities are different. It is clear that these polyurethanes do not show any measure of two phase scattering intensity pattern. Pure and well characterized domains of polyethylene glycol chains are thus apparently non existent. However the difference in the scattering pattern in these two polyurethanes, which differ only in the molecular weight, indicates a possible difference in the degree of organization of the soft segments. Higher intensity of scattering under the same conditions may be qualitatively related in this case to the higher degree of order, in analogy with the scattering pattern for two phase materials. It is to be



# Figure 31: SAXS Curves for KEH-600-6 and KEH-4000-6 Polyurethanes.

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noted that high molecular weight being conducive to the domain formation under otherwise identical conditions, the higher intensity of scattering for polyethylene glycol of molecular weight 600 as compared to 4000 may appear contradictory. But the number of the chains in the latter are about 6 to 7 times fewer compared to the former. The concentration of the chains surely has influence on the occurrence of the domains and their size. It is also noted that because of the lower stoichiometric requirement the effective isocyanate content available for the formation of the allophanate links is also high in KEH-4000-6.

#### Chapter VII

#### NETWORK MODIFICATION OF KRAFT POLYURETHANES WITH POLYBUTADIENE GLYCOL

#### 7.1 SYNTHESIS

Table 9 summarises the compositions of formulations used in the films. Terminology of the polyurethanes is based on the diisocyanates used for the synthesis (KBH- series for HDI and KBT- series for TDI).

In the use of polybutadiene glycol to incorporate soft segments into the network, two factors need to be mentioned in comparison to polyethylene glycols. With the use of excess diisocyanate, and hence limited build-up of molecular weight in the polyethylene glycol phase, difficulties had been noticed in increasing the glycol proportion in the synthesis of kraft polyurethanes. With polybutadiene glycol, no comparable difficulties were experienced, due to functionality in excess of two; in fact, networks were synthesized with the glycol as sole polyol component, for the purpose of comparison.

Secondly, in contrast to the synthesis of uniform films without visible nonuniformities with polyethylene glycols as components, kraft polyurethanes synthesized with this glycol were always found to develop inhomogeneities with the removal of solvent in the process of setting. Clear phase from the glycol base was either discrete or continuous depending on the composition. Polybutadiene glycol chains are thus

Composition of Kraft HPL - Polybutadiene Glycol Urethane Systems

Sample Designation	Polyol Co HPL wt.%	omponent Glycol wt.%	Isocyanate Component wt.%	NCO/OH Ratio
HDI Series				
KBH-2 KBH-10 KBH-6 KBH-5 KBH-7 KBH-11 KBH-8 KBH-12 KBH-13 KBH-9 KBH-1 KBH-4	83.3 71.4 67.8 64.3 53.6 35.7 17.8 7.1 3.6 0.0 0.0 0.0	0.0 0.0 3.6 7.1 17.8 35.7 53.6 64.3 67.8 71.4 80.0 83.3	16.7 28.6 28.6 28.6 28.6 28.6 28.6 28.6 28.6	$\begin{array}{c} 0.95 \\ 1.89 \\ 1.92 \\ 2.03 \\ 2.27 \\ 2.85 \\ 3.81 \\ 4.78 \\ 5.21 \\ 5.74 \\ 3.58 \\ 2.87 \end{array}$
TDI series				
KBT-1 KBT-8 KBT-6 KBT-3 KBT-5 KBT-5 KBT-7 KBT-7 KBT-9 KBT-2	71.4 67.8 64.3 53.6 35.7 17.8 7.1 3.6 0.0	0.0 3.6 7.1 17.8 35.7 53.6 64.3 67.8 71.4	28.6 28.6 28.6 28.6 28.6 28.6 28.6 28.6	1.83 1.89 1.96 2.19 2.75 3.68 4.61 5.03 5.55

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found to be incompatible, and this should have a major morphological bearing on the polyurethanes.

#### 7.2 THERMAL BEHAVIOR.

The glass transition temperature of the kraft polyurethanes modified with polybutadiene glycol are given in Table 10. The glass transition temperature goes through an initial minimum and then increases with weight contribution of the glycol. This is clearly observed for TDI polyurethanes; with HDI however, even though the trend does exist, difficulties were experienced in the detection of transition at high glycol concentrations.

It is clear that the trend observed in these polyurethanes is opposite to that observed when polyethylene glycols were used to incorporate soft segments. Though the effect of soft segments is apparent only at low levels of polybutadiene glycol, the behavior at high glycol concentrations can be reasoned along stoichiometric considerations. The polybutadiene glycol used has lower hydroxyl content (0.83 meq/g) compared to hydroxypropyl kraft lignin (2.52 meq/g). With the replacement of hydroxypropyl kraft lignin with polybutadiene glycol the isocyanate requirement of the polyol component decreases, and, as the weight content of isocyanate was kept constant in all the polyurethanes, the crosslink density is expected to increase. The initial decrease ir glass transition temperature indicates that at low

## Glass Transition Temperatures of Kraft Polyurethanes with Polybutadiene Glycol Soft Segments

Glycol wt.%	Polyurethane HDI	Based on TDI
0.0	158	158
3.6	85	122
7.1	106	130
17.8	94	137
35.7	94	162
53.6	NC	190
64.3	NC	200
67.8	NC	200

NC- No clear transitions observed in the temperature range.

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glycol contents, the effects of crosslink density are minor and are outweighed by the contribution to network flexibility due to the limited introduction of soft segments. At higher ranges however, the allophanate links due to excess diisocyanate can make the network more condensed than without any polybutadiene glycol and offset the effect of few strands of polybutadiene segments trapped into the lignin phase. At this point, it is interesting to compare two polyurethanes series- KT and KBT; the former without any soft segments. The glass transition temperatures of rubber modified polyurethanes (KBT) and of polyurethanes without such a modification (KT) are plotted in Figure 32 as functions of NCO/OH ratio. It is clear that there lies a striking between the  $T_{a}s$  at any NCO/OH correspondence ratio. The polyurethanes with polybutadiene glycol have а slightly lower temperature transition, and there is an apparent constancy in the decrease in glass transition temperatures because of soft segments. This probably reflects the modification of the lignin phase due to limited and constant miscibility of the glycol in the kraft lignin phase. However, it must be noted that the increase in the NCO/OH ratio in KT- series was due to higher proportions of diisocyanates used; but in KBT -series it was an effect of stoichiometry and employment of constant weight of diisocyanate.



Figure 32: Glass Transition Temperatures of Unmodified and Rubber Modified Kraft Polyurethanes.

#### 7.3 STRESS-STRAIN PROPERTIES.

Strength properties of the polyurethanes are given in Table 11. The compositional range studied for polybutadiene glycol modified kraft polyurethanes covered the entire range possible. The effects can thus be more clearly observed as opposed to polyethylene glycols where only lower weight fraction was employed.

modulus is Decrease in Young's observed with increasing polybutadiene glycol content. TDI based polyurethanes, also have higher moduli than the HDI polyurethanes. The decrease is smoother in case of HDI series than in TDI series. Both the series show a corresponding decrease in tensile strength. It appears that polyurethanes with up to 35.7% the glycol (this corresponds to 50% of the polyol component) are significantly different in tensile properties from polyurethanes with still higher concentrations. The ultimate strain values are not much different from, and in some cases are lower than pure kraft polyurethanes, when glycol is employed as a component in polyol up to the concentration of 35.7%. With higher glycol contents, the extensibility of the films increases markedly, and the tensile characteristics in general reflect the effect of the rubbery phase and its lower load bearing capacity.

The decrease of the modulus in both KBH and KBT series at very high concentrations of the rubber are evidently due to change in the nature of the system from being rich in rigid lignin structures at one end to the one with flexible chains of polybutadiene at the other. The

Tensile Properties of Polybutadiene Glycol Modified Polyurethanes

Sample	Kraft HPL wt.%	Young's Modulus MPa	Ultimate Stress MPa	Ultimate Strain %
HDI Series				
KBH-10 KBH-6 KBH-5 KBH-7 KBH-8 KBH-12 KBH-13 KBH-9 KBH-1	71.4 67.8 64.3 53.6 17.8 7.1 3.6 0.0 0.0	$1671\pm511219\pm701373\pm701060\pm93208\pm554\pm445\pm748\pm836\pm11$	73.5 43.7 34.5 24.5 4.3 6.3 6.5 8.1 7.2	6.8 5.1 3.1 2.6 4.0 62.4 76.7 140.0 159.0
TDI series				
KBT-1 KBT-8 KBT-6 KBT-5 KBT-4 KBT-7 KBT-9 KBT-2	71.4 67.8 64.3 35.7 17.8 7.1 3.6 0.0	2076±318 1789±46 1785±134 634±39 51±4 36±4 45±6 52±8	48.5 62.9 43.5 24.4 5.1 4.8 8.6 8.9	6.0 4.7 3.7 6.1 38.0 68.0 130.0 171.0

ultimate properties show the expected behavior near either extremes. However, it is important to note that despite increase in crosslink density with increase in glycol content, there are significant effects due to soft segment incorporation. This observation is similar to the one on KEH-series with polyethylene glycol of molecular weight 4000.

#### 7.4 SCANNING ELECTRON MICROSCOPY

The polyurethanes were studied with scanning electron microscopy as the phase separation was evident at a macroscopic level. The features were examined both at the surface of the cast film as well as along the fracture surfaces to examine the bulk structure as related to the surface.

Figure 33 shows the features of two polyurethanes KBH-6 and KBT-8. Both have polybutadiene glycol weight fraction of 3.6%. The phase separation is thus seen to exist, even at the lowest weight fraction of the glycol when based on HDI. The SEM of the fracture surface also indicates that polybutadiene glycol network exists as incompatible phase suspended in kraft polyurethane network. KBT-8 on the other hand does not show any comparable features. Figure 38 illustrates the phase structure at a higher magnification and the bonding between the two phases is noticeable in KBH-6 despite the clear boundary separation. The same observation is forthcoming from the SEMs of KBH-5 and KBT-6 (Figure 34). The glycol content in these

two polyurethanes is 7.1% and the the onset of phase separation is noticeable in KBT-6. The sizes of the domains in KBH-5 are larger as compared to KBH-6. The same trend is observed when glycol weight fraction is increased to 17.8 and 35.7% as revealed in Figure 35 and 36.

The fracture surfaces of the polybutadiene glycol and lignin polyurethane phase show a distinct difference (Figure 37). The rubbery phase fracture is accompanied by the retraction of the matrix in the form of globules on the surface. On the other hand the glassy lignin phase shows only the dilatation effects as is characteristically seen in epoxies.<sup>114</sup> Figure 39 shows the existence of extensive pore structure in polybutadiene glycol rich polyurethanes. KBT-3 has a comparatively low glycol concentration (17.8%) and the onset of pore structure in the rubbery phase is noticed. As the concentration of this phase increases (as in KBT-4 with 53.6% and KBT-7 with 64.3%), the porous nature becomes more and more predominant. The pore structure was also noticed, when the films were examined under polarizing microscope.

On the basis of these micrographs, it is evident that polybutadiene chains exhibit a high degree of incompatibility with hydroxypropyl kraft lignin. Limited miscibility of these chains in the kraft polyurethane network has been inferred from the results of thermal analysis. Moreover, in regard to stress-strain behavior, polyurethanes with low polybutadiene glycol content (up to 50% of the polyol component), showed significantly different properties from those with higher content

of polybutadiene glycol, with a discontinuity in between. This is in contrast to polyurethanes with polyether chains, where the films showed no signs of inhomogeneity at any composition or molecular weight examined, and there was a smooth variation in properties. At this stage it is reasonable to conclude that in order to incorporate the soft segments in kraft polyurethane matrix, there is a certain requirement of intermolecular affinity arising due to such polarity effects as hydrogen bonding. It is probable that polyether chains from glycols are easily distributed in the network due to hydrogen bonding between urethane bonds and the polyether oxygen, and previous work on this aspect influencing the domain structure of thermoplastic polyurethanes tends to support this inference.<sup>53</sup>

#### 7.5 DYNAMIC MECHANICAL ANALYSIS.

The dynamic mechanical spectra of polybutadiene glycol modified kraft polyurethanes (KBH-6 and KBH-8) are shown in Figures 40 and 41. KBH-6 and KBH-8 have 3.6 and 53.6 weight<sup>6</sup> glycol respectively, which amounts to approximately 5 and 75% of the polyol fraction. Thus these two polyurethanes represent two extremes in composition, the latter being largely rubber. KBH-8 shows a clear polybutadiene glycol transition at -60°, close to the homopolymer. This is hardly observed in KBH-6. The peak value of tan<sup>§</sup> for KBH-6 occurs at about 120°C and is slightly larger in magnitude and broader compared to pure kraft Figure 33: SEMs of Surface and Fracture Surface of KBH-6 (a,b) and KBT-8 (c,d).


Figure 34: SEMs of Surface and Fracture Surface of KBH-5 (a,b) and KBT-6 (c,d).



Figure 35: SEMs of Surface and Fracture Surface of KBH-7 (a,b) and KBT-3 (c,d).



Figure 36: SEMs of Surface and Fracture Surface of KBH-11 (a,b) and KBT-5 (c,d).



Figure 37: Mode of Fracture of Lignin (a) and Polybutadiene (b) Phases.



Figure 38: SEMs of Surface and Fracture Surface of KBH-6 (a,b) and KBT-6 (c,d).



Figure 39: SEMs of Polyurethanes With High Polybutadiene Glycol Content KBT-3 (a,b), KBT-4 (c) and KBT-7 (d).



polyurethane, KH-4. The modulus begins to fall around 30°C for KBH-6, whereas it is fairly stable for KH-4. However, the behavior beyond glass transition is similar in both cases and modulus approaches a stable value. KBH-8 on the otherhand, indicates a characteristic rubbery network. The moduli values are considerably lower than KBH-6 and two distinct transitions are observed. The one around -50°C clearly originates from polybutadiene phase. Rubbery plateau is observable between this transition and the one originating from lignin phase. The latter transition occurs at a significantly higher temperature as compared to KBH-6, and the modulus continues to drop without reaching a stable value till the end of the temperature program (200°C).

The stabilization of modulus beyond glass transition, in case of KBH-6, indicates a crosslinked network. The decrease in modulus while approaching glass transition for KBH-6 may be due to a fraction of polybutadiene chains trapped in the lignin phase. It can be recalled that the existence of the domains of rubber suspended in lignin phase is proved beyond any reasonable doubt in KBH-6, with scanning electron microscopy. It may be surprising that the transition for this phase is hardly discernible. It is possible that this could be a result of a low magnitude of the drop in modulus at the glass transition. The average drop in the modulus at glass transition is about three decades. The drop in the modulus at  $-60^{\circ}$ C for KBH-8 is hardly a decade. Comparison of the magnitude of the tan of the tan for rubber and lignin



Figure 40: Dynamic Mechanical Spectrum of Polyurethane KBH-6.



Figure 41: Dynamic Mechanical Spectrum of Polyurethane KBH-8.

transition is about the same, yet with fifteen times the weight fraction in the former, thus pointing to the difficulty in the detection of transitions arising from this phase in the dynamic mechanical spectrum.

## Chapter VIII

## CONCLUSIONS

The study on synthesis and characterization of polyurethanes based on (HPLs), demonstrated that hydroxypropyl lignins properties of polyurethane networks can be significantly modified by control of synthesis variables, and incorporation of soft segments from straight The utility of network modification by introducing chain glycols. structures with flexibility has been tested before, in case of epoxies. The relevance of this concept to lignin based polyurethanes is especially important, due to rigid nature of products originating from highly aromatic and polyfunctional nature of the materials. Following conclusions are drawn from this study.

- Hydroxypropylation serves as a valuable chemical modification procedure to improve the solubility characteristics of lignins, in reducing the differences in the reactivity of the functional groups, and in converting the lignins into polyester-ether polyol suitable for the synthesis of thermosetting polyurethanes.
- 2. The preliminary investigation on the polyurethane films synthesised by use of monomeric diisocyanates and hydroxypropylated lignins demonstrates the utility of the solution casting procedure in providing materials suitable for

mechanical testing. The limitations in the testing of mechanical properties of lignins has been due to their powdery nature and this procedure overcomes this problem by the synthesis of networks of sufficient strength.

- 3. The thermosetting characteristics in the polyurethanes in lignin originate not only from the multifunctionality of the HPLs, but also by use of excess diisocyanate. The latter produces primary crosslinks with allophanate bonds and is seen to have a predominant effect on the glass transition temperature.
- 4. The rigidity characteristics of the polyurethanes from macrocyclic lignin oligomers depend on the diisocyanate used. Comparison of hexamethylene diisocyanate (HDI) and tolylene diisocyanate (TDI) show that straight chain characteristics of the diisocyanate have a controlling influence on the thermal and mechanical properties.
- 5. Glass transition temperatures of the polyurethanes increase generally in proportion to the NCO/OH ratio. This trend is polyurethanes. observed clearly in TDI based In HDI polyurethanes however, the increase is confined only to the lower range. As the ratio is increased further the glass transition temperature drops. At this stage it is concluded that the straight chain incorporation by the diisocyanate probably overrides the contribution to crosslink density due to the formation of allophanate bonds.

- 6. Use of excess diisocyanate had apparently no detrimental effect on the mechanical properties of the polyurethanes produced with HDI. With TDI however, the actual NCO/OH ratio may influence the properties very strongly and thus practically limit the isocyanate content, in the synthesis of testable materials.
- 7. Polyethylene glycols of molecular weight 400-4000 are observed to be fully compatible with hydroxypropyl lignin in the synthesis of polyurethanes. The soft segments introduced bring about an increased flexibility and result in lowering the temperature of mechanical relaxation and thermal transition.
- 8. The glass transition temperatures are significantly lowered in these network polyurethanes with inclusion of glycols. The drop is proportionate to the glycol content of the system. However this is also subject to network crosslink density effects.
- 9. The structure of diisocyanate (aromatic vs. aliphatic) has a dominant effect on the extent of drop in glass transition temperature of lignin based thermosets. Due to aromatic nature, transition temperatures of TDI polyurethanes were invariably higher than HDI polyurethanes, under otherwise identical compositions.

- 10. A three to four fold decrease in modulus, and up to five fold increase in elongation is observed by incorporation of soft segments, in amounts up to 25 percent of the polyol weight. The extent of influence in any polyurethane was a combined effect of glycol content, crosslink density and the nature of diisocyanate.
- 11. The energy dissipation characteristics, as measured by tanδ in the dynamic mechanical spectrum, are functions of both the contribution to weight by the soft segments as well as the crosslink density of the system. With both factors favoring, the internal friction increased for PEG 600, and, with crosslink density dominating, decreased for PEG 4000.
- 12. Dynamic mechanical spectra of the polyurethanes with polyethylene glycols as components fail to show any clear transitions ascribable to soft segments. This is probably the result of network characteristics of the system as well as the low concentration of organizable soft segments. However, it is noted that an additional transition, not present in pure kraft polyurethane, is observed in the spectra of these polyurethanes.
- 13. The crosslink density effects accompanying the increase in molecular weight (because of constancy maintained in the excess

diisocyanate), make it difficult to decouple the effects of molecular weight and composition. However, with a proper selection of component glycol and minimum excess of diisocyanate, it is possible to introduce a considerable measure of thermoplasticity into these thermosetting systems

- 14. The incompatibility of soft segments with hydroxypropyl lignins can be a dominant factor in the homogeneity of the polyurethanes. Polybutadiene glycol, by virtue of hydrophobic nature of the chains, produces very nonuniform polyurethanes with macrophase separation.
- 15. The glass transition temperatures of rubber modified kraft polyurethanes (with polybutadiene glycol) show opposing trend with rubber concentration as compared to polyethylene glycols. The low stoichiometric requirement of the former, in conjunction with incompatibility of the chains, produces more condensed domains of lignin with lightly crosslinked polybutadiene glycol phase remaining suspended in the matrix of kraft polyurethane network.
- 16. Only marginal differences in thermal and mechanical properties are observed in polybutadiene glycol polyurethanes in comparison to polyethylene glycol polyurethanes at comparable compositions. This is attributed to limited miscibility of the polybutadiene glycol chains with hydroxypropyl lignin.

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## Appendix A



Figure 42: FT-IR Spectrum of Kraft Lignin



Figure 43: FT-IR Spectrum of Hydroxypropylated Kraft Lignin



Figure 44: FT-IR Spectrum of lotech Lignin







Figure 46: Proton NMR Spectrum of Acetylated Kraft Lignin.



Figure 47: Proton NMR Spectrum of Acetylated Kraft HPL.



Figure 48: Proton NMR Spectrum of Acetylated lotech Lignin.


Figure 49: Proton NMR Spectrum of Acetylated lotech HPL.

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