CHAPTER II

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ABSTRACT

Esterification of organosolv lignin to lignin acetate, butyrate, hexanoate and laurate was performed using acid anhydride and acyl chloride reactions. On average, 0.69 to 0.87 acyl groups per C₉-unit were introduced according to ¹H-NMR results. The molecular weight increased with increasing ester chain length, and a narrow molecular weight distribution was observed for lignin laurate. The substitution of the hydroxyl groups of lignin with the acyl substituents decreased the glass transition temperature of the lignin esters primarily due to the increase in the free volume. The decrease in the glass transition was proportionate to the number of carbon atoms in the acyl substituent.

INTRODUCTION

Lignin has network-like behavior in biomass, and it possesses extensive branching when isolated from delignification solutions. It is obtained from almost all types of plant resources. It is separated from the cellulose conventionally either by strong alkaline or acidic solutions, or by a high pressure steam treatment followed by solvent extraction.



Organosolv Lignin

 R_1 mostly OCH₃, H or other unit R_2 mostly OCH₃ R_3 mostly OH or other unit R_4 mostly other unit

Unmodified lignin often possesses poor solubility and thermoplastic melt flow characteristics like cellulose. Similar to thermoplastic cellulose ester derivatives, one method adopted in order to improve the properties and use of lignin as a thermoplastic polymer is by esterification. Esterification of lignin has been known since the late forties when it was found to be useful as a mold lubricant and possessing characteristics of melting point and solubility [Lewis and Brauns (1947)]. More studies were carried out by Glasser and Jain on unmodified and bleached lignin esters [Glasser and Jain (1993)]. Enhanced solubility and melt characteristics along with a reduction in glass transition temperature and improved thermal decomposition behavior were reported for lignin alkanoates. Moreover, bleaching with acetic acid and H₂O₂ led to an increase in molecular weight (M_n) and a narrower molecular weight distribution possibly due to the preferential removal of low molecular weight species. Studies on molecular weight distribution of semi-commercial lignin acetates exhibited more or less uniform distributions of weight average molecular weights (M_w) and high molecular weight distributions (between 2 and 12) [Glasser, Dave and Frazier (1993)]. However, compatibility of the lignin esters with the other components of the blend systems are to be established before it can be used for applications in blends with other thermoplastic polymers.

Acylation can be carried out with the use of acyl chlorides or acid anhydrides [Vogel (1989)]. Acylations with acid anhydrides or acyl chlorides are carried out in the

presence of suitable acid catalysts, such as sulphuric acid or zinc chloride, or using a basic catalyst, such as pyridine. The reactions with acyl chlorides and acid anhydrides are represented below.



However, the large scale acylation procedure of lignin may most efficiently parallel that of the esterification of cellulose on industrial scale. On an industrial scale, the esterification reaction is carried out by the use of a mixture of the alkanoic acid and the respective anhydride along with a metal (sodium or potassium) alkanoate catalyst. The reaction takes place under relatively severe conditions (high temperature). This leads to the drastic reduction of the reaction time.

This chapter deals with the preparation and analytical characterization of the lignin esters. Lignin acetate (LA), lignin butyrate (LB), lignin hexanoate (LH) and lignin laurate (LL) were prepared from organosolv lignin, and these esters have been utilized for the compatibility studies with some biodegradable polymers covered in the later chapters of this thesis.

EXPERIMENTAL

MATERIALS

Organosolv Lignin (L) was obtained from Aldrich Chemical Company, WI, USA (Catalog #: 37,101-7). The glass transition temperature (measured by differential scanning calorimetry) and thermal decomposition temperature (measured by thermogravimetric measurements) are 107^{0} C and 308^{0} C, respectively. Number and weight average molecular weights, M_n and M_W are 350 and 1230 respectively with a MWD of 3.5. The powder was dried under vacuum at 40° C for 12 hours before use.

METHODS

The esterification reactions and precipitation methods were adopted from earlier published literature [Glasser and Jain (1993); Glasser, Dave and Frazier (1993)].

• Esterification Reaction for LA, LB and LH

Lignin (25 - 40 gms) was stirred in ca. 125 ml of distilled (dry) pyridine at room temperature under a dry nitrogen atmosphere until all the lignin was dissolved. The solution was cooled to 0^{0} C and the corresponding acyl anhydride (ca. 1.5 times the molar amount of lignin, assuming a C₉-unit weight of 191 representing a mole of lignin) was added drop-wise at ice temperature. The reaction mixture was then slowly heated to room temperature and the reaction was allowed to proceed with stirring for 48 hours at room temperature.

Precipitation and Separation of LA, LB and LH

The reaction mixture was precipitated in 10 times non-solvent (water) containing 1% sodium bicarbonate solution. The bicarbonate solution was kept at room temperature for the precipitation of lignin acetate and butyrate; in contrast, the bicarbonate solution was heated to 60 $^{\circ}$ C before precipitating lignin hexanoate, since the longer chain fatty acids are not readily soluble in water at room temperature. The reaction mixtures were added dropwise with fast stirring and allowed to stir for 4–16 hours. They were then filtered and the precipitates were washed with 0.1 N hydrochloric acid solution to remove pyridine. The mixtures were filtered and washed repeatedly with water to remove any acid. The final filtrate was dried in a vacuum oven at 45°C for 24 hours to remove any residual water and then stored in tightly sealed containers.

Esterification Reaction for LL

Lignin (50 gms) was stirred in 250 ml of dry pyridine at room temperature under a dry nitrogen atmosphere until all the lignin was dissolved in pyridine. The solution was cooled to ice temperature (0° C) and lauroyl chloride (100 ml) was added dropwise from an addition funnel with constant stirring of the reaction mixture. The reaction mixture was then slowly heated to room temperature and the reaction was allowed to proceed with continuous stirring for 48 hours at room temperature.

• Precipitation and Purification of LL

Owing to low solubility of lauric acid in aqueous bicarbonate, precipitation of the lignin laurate mixture in bicarbonate solution failed to separate lignin laurate from the other impurities and a thick viscous tar-like material was obtained. Therefore, solventsolvent extraction was adopted to separate lignin laurate from the reaction mixture. The reaction mixture was dissolved in chloroform and solvent-extracted with sodium bicarbonate solution in an extraction funnel. Pyridine and acids present in the reaction mixture were partitioned from the chloroform phase to the water phase. The extraction was repeated several times (5 to 6 times) to remove most of the lauric acid. An intermediate layer, possibly containing the sodium salt of the fatty acids, was formed while extracting. Small amounts of sodium hydroxide (NaOH) solution were also added to neutralize the fatty acids remaining in the chloroform layer. However, large amounts of NaOH should not be used as that might lead to de-esterification of lignin laurate. The chloroform phase was repeatedly extracted with water, and the chloroform phase containing lignin laurate was separated. Chloroform was removed by roto-evaporating the extracted chloroform phase. However, characterization of this products by FTIR and DSC (not shown) revealed the presence of lauric acid along with lignin laurate. It was observed that lignin laurate was soluble in acetone whereas lauric acid was insoluble. Hence, lauric acid was removed from lignin laurate by dissolution of the product in acetone, followed by removal of acetone by evaporation. Lignin laurate was obtained as a thick black-colored tar.

FTIR Analysis

Fourier transform infra-red (FTIR) spectra were recorded on a Nicolet 5SXC spectrophotometer using KBr pellets.

NMR Analysis

The proton nuclear magnetic resonance (¹H-NMR) spectra were obtained using a 270 MHz Bruker WP-270 spectrometer. The samples were dissolved in deuterated chloroform and filtered by glass wool before transferring to the NMR tubes. The number of scans for the samples in the NMR was 16.

Molecular Weight Determination

Molecular weights were determined by gel permeation chromatography (GPC). GPC was perfomed on a set of 3 UltrastyragelTM columns with gel sizes of 10^3 , 10^4 and 10^6 A using a Waters instrument in non-stabilized tetrahydrofuran. Both differential refractive index (Waters 410) and differential viscosity (Viscotek Model No. 100) detectors were employed in sequence. The flow rate was 1.0mL min⁻¹ and the calculations were based on the Trisec calibration-narrow curve.

Differential Scanning Calorimetry

The thermal analysis of the samples was determined on a Perkin-Elmer Model DSC-4 equipped with a Thermal Analysis Data Station (TADS) using standard aluminum

pans. Measurements were made on ca. 10 mg samples in the temperature range between – 20 and 180°C at a scanning rate of 10°C/min. Nitrogen was used as a sweeping gas. The instrument was calibrated with an indium standard. The glass transition temperature was reported from the second heating scan, unless otherwise indicated. The glass transition temperature (T_{o}) was taken as the temperature at the midpoint (1/2 ΔC_{p}) of the transition.

RESULTS AND DISCUSSION

CHEMICAL STRUCTURE

Chemical structure analysis of lignin esters can be effectively judged by FTIR and NMR as described in earlier publications [Glasser and Jain (1993)]. In case of FTIR, acylation is revealed by the appearance of the ester peaks at around 1765 and 1740 cm^{-1} corresponding to the aromatic and aliphatic alkanoxy groups respectively (Fig. 2.1 and 2.2). The fraction of the aromatic to aliphatic substitution of OH groups by the acyl substituent group can be quantitatively determined by the peak ratios of the 1765 to the 1740 cm⁻¹ bands [Schultz and Glasser (1986)]. These peaks are illustrated in Figure 2.2 and the values are plotted in Figure 2.3. Significant difference is observed in the amount of -CH₂ substituents present in the lignin ester. The CH₂ substituents show in the peaks around 2960 cm⁻¹ due to the CH stretching band in methyl and methylene groups. The relative amounts of CH₂ substituents can be determined by the ratio of 2960 to 1510 cm⁻¹ peak heights, since the 1510 cm⁻¹ band, which is attributed to the aromatic ring vibrations, is considered as a constant value for all the lignin esters. A plot of the ratio of 2960 to 1510 cm⁻¹ (Figure 2.4) reveals that the amount of CH_2 substituents in the ester increases as the ester length increases from C_2 (in acetate) to C_{12} (in laurate). This approximate linear relationship between the peak ratios and the number of carbon atoms is consistent with the expected results.

The other method to determine the structure of the lignin esters is by solution ¹H-NMR spectroscopy [Glasser and Jain (1993)]. Broad proton signals are displayed in the regions where little interference exists with other proton signals. The total acyl content can, therefore, be calculated on the basis of these signals. The ¹H-NMR spectrum of organosolv lignin reveals the protons in methoxyl groups (OCH₃) peak near 3.76 ppm. This corresponds to 3.33 aliphatic H per C₉-unit for hardwood lignin and this value is the basis for the calculations (Fig. 2.5) [Glasser et.al.(1981)]. The other distinguishable chemical shifts are near 8.0 to 6.2 ppm (δ values) due to the aromatic proton in guaiacyl and syringyl units [Glasser and Kelley (1987)]. The value for the aromatic H per C_9 -unit for hardwood lignin is 2.15 [Glasser and Jain (1993)]. The signals at 7.26 ppm and 1.26 ppm are due to the chloroform solvent and the highly shielded aliphatic H respectively. The spectrum for lignin acetate has two extra peaks, near 2.3 and 2.15 ppm, and these are due to the aromatic acetate and aliphatic acetate H respectively as mentioned in earlier publications (Fig. 2.6). In case of lignin butyrate, four additional peaks are observed related to the aromatic and aliphatic H from the CH₂ groups distant from the carbonyl group as shown in Figure 2.7. However, the contributions to the chemical shifts from the CH₂ groups distant from the carbonyl group become more pronounced when the length of the ester substituent increases from butyrate to laurate. Therefore, the signals corresponding to the CH₂ groups further away from the carbonyl group for hexanoate and laurate are correspondingly higher compared to those from the closer CH₂ groups (Fig. 2.8 and 2.9).

The fraction of the aromatic acyl substituent out of total acyl substitution calculated by FTIR and NMR are represented in Table 2.1. The values are between 0.53 and 0.64 varying due to analytical techniques and accuracy of interpretation. The degree of substitutions (DS) or acyl content per C_9 unit were in the range of 0.69 to 0.87 for different lignin esters.

MOLECULAR WEIGHTS

The determination of the molecular weight and the associated parameters of lignin and lignin derivatives poses a problem even with advanced analytical methods [Glasser and Kelley (1987)]. However, the use of high pressure gel permeation chromatography using non-aqueous solutions along with differential viscosity detectors have shown better results in molecular weight determination of lignin and its derivatives [Glasser and Jain (1993)]. Choice of solvent has been THF over DMF-LiBr and the calibration technique has been based on polystyrene standards or on lignin-like model compounds [Glasser and Kelley (1987)]. Detailed molecular weight analysis of lignin acetates is covered in an earlier paper [Glasser, Dave and Frazier (1993)]. The various molecular weights and the polydispersity of each lignin ester have been summarized in Table 2.2. The molecular weights increase with the increase in the length of the ester substituent as shown in Figure 2.10. This increase is not primarily due to the increase in the length (and hence molecular weight) of the ester substituent from C_2 (in acetate) to C_{12} (in laurate). Earlier publications have attributed this difference between the theoretical and experimental molecular weights for lignin derivatives to the change in hydrodynamic volume [Kelley and Glasser (1988)]. This difference is also presented in Table 2.2 and confirms to the fact that the Mark Houwink Sakurda constant 'a', in fact, increases with the increase in ester substituent length. However, decreased solubility and exclusion of the lower molecular weight species for the longer ester substituent (lignin laurate) can also affect the molecular weight determination to certain extent. However, it can be observed that the molecular weight distribution decreases for the lignin laurate as compared to the acetate, butyrate and hexanoate (Fig. 2.11). This reveals a decrease in the polydispersity of the lignin with the possible degradation or exclusion of the lower molecular weight species during reaction with lauroyl chloride. These differences observed in the molecular weight distribution may be also attributed to the different reaction methods adopted. Lignin laurate was prepared by the acyl chloride method whereas, the other lower chain esters were prepared by the corresponding acid anhydride reaction.

GLASS TRANSITION TEMPERATURE

The glass transition in this study is taken to be the midpoint of the transition. The transitions as observed by the second scans of the DSC are shown in Figure 2.12. The glass transitions for the acetate, butyrate, and hexanoate were clear, whereas the glass transition of lignin laurate was not clearly distinguished. However, the glass transition of lignin laurate is assumed to be in the middle portion of the enthalpy gradient as shown by the arrow mark. Other analysis techniques such as dynamic mechanical tests have to be employed to determine the glass transition of LL. The glass transition values for each of the lignin esters have been plotted against the number of carbon atoms in acyl substituent in Figure 2.13. It is observed that the glass transition temperature decreases to lower values as the length of the ester substituent increases. This decrease in the glass transition is essentially due to the increase in the free volume of the molecules as the ester substituent increases. The concentration of chain ends resulting from the replacement of the hydroxyl groups by the acyl substituents as well as the length of the acyl substituent, contribute to an increase in free volume of the lignin esters. This behavior has also been

noted earlier in case of lignin esters [Glasser and Jain (1993), Lewis and Brauns (1947)] and cellulose esters with smaller ester substituents (C_6 or lower) [Sealey et.al. (1996)]. Another explanation for the T_g depression may be the elimination of hydrogen bonds due to the substitution of hydroxyl groups in lignin by ester substituent (as explained by Sealey et. al. in case of cellulose esters). This leads to increased mobility within the lignin molecules and hence depression of the glass transition to lower temperatures. Comparison of the data provided by Glasser and Jain (1993) on bleached lignin esters reveal consistency in the nature of the curves (Fig. 2.13). This implies a similar effect of the length of the ester substituent on the glass transition depression of lignin.

CONCLUSION

The chemical structure of the lignin derivatives (LA, LB, LH and LL) have been analyzed by FTIR and NMR. On an average 0.69 to 0.87 acyl groups were introduced per C_9 unit. The ratio of 2960 to 1510 cm⁻¹ reveals a linear correlation to the number of carbon atoms in the ester substituent. The molecular weights increases as the ester substituent length increases from acetate to laurate. A narrower molecular weight distribution is observed in case of lignin laurate as compared to the lower substituent size esters considered. The glass transition temperatures are significantly reduced to lower temperatures as the chain length of the ester substituent increased, possibly due to the change in the free volume of the molecules. This reduction in glass transition temperatures is consistent with other studies reported in the literature.

REFERENCES

- Glasser, W. G., Dave, V., and Frazier, C. E., (1993), "Molecular Weight Distribution of (Semi-) Commercial Lignin Derivatives," Journal of Wood Chemistry and Technology, 13(4), 545-559.
- Glasser, W. G., and Jain, R. K. (1993); Lignin Derivatives I. Alkanoates, *Holzforschung*, 47, 225-233.
- Glasser, W. G. and Kelley, S. S. (1987), Lignin, *Encyclopedia of Polymer Science and Engineering*, Vol. 8, Second Edition, pp. 795-852, John Wiley & Sons, Inc.
- Glasser, W. G., Glasser, H. R. and Morohoshi, N. (1981); Simulation of Reactions with Lignin by Computer (SIMREL). 6. Interpretation of primary Experimental Analysis Data ("Analysis Program"). *Macromolecules* 14, 253-262.
- Irvine, G. M. (1984); The Glass Transitions of Lignin and Hemicellulose and their Measurements by Differential Thermal Analysis, *TAPPI*, 67(5), 118-121.
- Kelley, S. S. and Glasser, W. G. (1988), "Engineering Plastics from Lignin XIV. Characterization of Chain-Extended Hydroxypropyl Lignins", *Journal of Wood Chemistry and Technology*, 8(3), 341-359.
- Lewis, H. F. and Brauns, F. E. (1947), Esters of Lignin Material, U.S. Patent # 2,429,102.
- Schultz, T. P. and Glasser, W. G. (1986), Quantitative Structural Analysis of Lignin by Diffuse Reflectance Fourier Transform Infrared Spectrometry, *Holzforschung*, 40 (Suppl.), 37-44.
- Sealey, J. E.; Samaranayake, G.; Todd, J. G., and Glasser, W. G., (1996), "Novel Cellulose Derivatives. IV. Preparation and Thermal Analysis of Waxy Esters of Cellulose," Journal of Polymer Science: Part B: Polymer Physics, Vol. 34, 1613-1620.
- Vogel's Textbook of Practical Organic Chemistry (1989), by Furniss, B. S., Hannaford, A. J., Smith, P. W. G. and Tatchell, A. R., Longman Scientific & Technical, Essex, England, Chapter 5, pp.5.12, 5th edition.

	Fraction o substituen	Acyl Content of		
	FTIR ¹	NMR ²	by H-NMR	
Organosolv lignin acetate	0.59	0.64	0.82	
Organosolv lignin butyrate	0.56	0.61	0.69	
Organosolv lignin hexanoate	0.53		0.87	
Organosolv lignin laurate	0.54		0.81	

Table 2.1 : Chemical structure analysis of lignin esters

¹ Determined by the peak height ratios of 1765 to the total peak height of 1765 and 1740 as illustrated in Fig.2.2.

² Determined by the ratios of the peak areas for the aromatic substituents to the total (aromatic and aliphatic) substitution as illustrated in Fig 2.6 for lignin acetate.

Lignin Ester	Experimental Values		Theoretical Values **		Exp. MWD	Mark Houwink Sakurda	T_g
	M _n	$M_{\rm w}$	M _n	$M_{\rm w}$		Constants	(C)
Organosolv Lignin	820	3,140	764	2682	3.83	a = 0.148 Log K = -2.253	107
Lignin Acetate	1,550	5,890	901	3352	3.80	a = 0.204 Log K = -2.536	92
Lignin Butyrate (unbleached)	2,310	7,730	955	3180	3.34	a = 0.218 Log K = -2.591	52
Lignin Butyrate* (bleached)	5,450	18,400	-	-	3.38	a = 0.196 Log K = -2.940	93
Lignin Hexanoate	2,650	9,440	1105	3923	3.56	a = 0.222 Log K = -2.585	30
Lignin Laurate	13,400	33,200	1353	3288	2.48	a = 0.269 Log K = -3.207	2

Table 2.2 :	Molecular	weights	and glass	s transition	temperature	values for	or different	lignin
	esters.							

* Glasser and Jain (1993)

** Theoretical M_n values are calculated taking a C_9 – unit weight of 191 for organosolv lignin and a DP_n of 4.0. Corresponding degree of substitution (DS) values for different lignin esters are taken from Table 2.1. Theoretical M_w is reported as the product of M_n and molecular weight distribution (MWD).



Figure 2.1 : FTIR results of lignin esters



Figure 2.2 : Representative FTIR plot for lignin butyrate depicting the various peaks used for calculations in the study.



Figure 2.3 : Ratio of 1765 to 1740 cm⁻¹peak heights provides information on the fraction of aromatic to aliphatic substituted OH groups in lignin esters.



Number of C atoms in the ester substituent





Figure 2.5: ¹H-NMR spectra of organosolv lignin in D-CHCl₃



Figure 2.6 : ¹H-NMR spectra of organosolv lignin acetate in D-CHCl₃



Figure 2.7 : ¹H-NMR spectra of organosolv lignin butyrate in D-CHCl₃



Figure 2.8 : ¹H-NMR spectra of organosolv lignin hexanoate in D-CHCl₃



Figure 2.9: ¹H-NMR spectra of organosolv lignin laurate in D-CHCl₃



Number of C atoms in the ester substituent

Figure 2.10 : Plot of number average molecular weight of different lignin esters.



Number of C atoms in the ester substituent

Figure 2.11 : Plot of the molecular weight distribution for each lignin ester



Figure 2.12 : DSC thermograms of different lignin derivatives. These traces are from the second heating scan (after quenching from melt). (L - Lignin, LA- Lignin Acetate, LB-Lignin Butyrate, LH- Lignin Hexanoate, LL - Lignin Laurate.)



Figure 2.13 : Variation of glass transition temperature of different lignin ester derivatives as a function of carbon atoms in the ester group substituents.

* Reproduced from Glasser and Jain (1993)