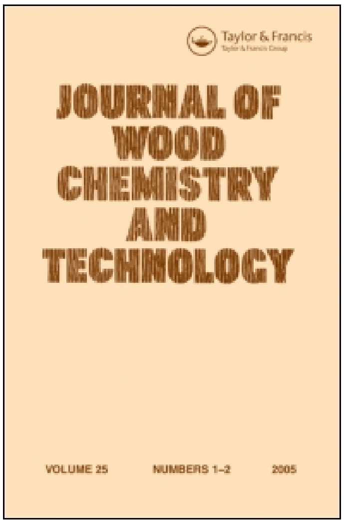

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Engineering Plastics from Lignin XIV. Characterization of Chain-Extended Hydroxypropyl Lignins

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ENGINEERING PLASTICS FROM LIGNIN
XIV. CHARACTERIZATION OF CHAIN-EXTENDED HYDROXYPROPYL LIGNINS

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ABSTRACT

Three series of chain-extended hydroxypropyl lignins (CEHPLs), prepared from organosolv and kraft lignin, were examined regarding their chemical, molecular weight and thermal characteristics. Results showed that the molar substitution (MS) of propylene oxide, which was defined as the number of propoxy repeat units which comprise the chain attached to a single reactive site on lignin, varied and affected copolymer properties. As the MS increased from 1 to 7.2, the number average molecular weight ($\overline{M}_n$) increased while the glass transition temperature (T_g) decreased. The actual $\overline{M}_n$ observed by GPC exceeded however that expected on the basis of mass gain by derivatization. This was attributed to changes in the apparent hydrodynamic volume in relation to MS. The change in T_g with increasing MS followed the Gordon-Taylor relationship. Differences in the chemical composition of the original lignin (organosolv or Kraft) were not obvious as the lignin content of the copolymer decreased below 50%.

INTRODUCTION

Lignin has been reacted with a series of alkylene oxides[1-3] to yield star-like polyols which can be crosslinked in a variety of ways[4-7]. Lignin reacted with propylene oxide (PO) displayed improved solubility and lower temperature transitions[8]. Hydroxypropyl lignins (HPLs) have been crosslinked with diisocyanates to produce polyurethane films, coatings and foams[4,5]. While these products showed high modulii and strengths they were brittle and had poor elongation[4]. In an effort to overcome these limitations, a series of polyethylene glycol (PEG)[9] and polybutadiene glycol-extended polyurethanes[10] were prepared with HPL. While these flexible extenders improved the elongation of the subsequent polyurethanes they were limited by either the glycol content or by phase separation. In order to prepare homogeneous, lignin-based polyurethanes with a large percentage of the flexible component, PO chain-extended hydroxypropyl lignins (CEHPLs) were synthesized. Thus, while the degree of substitution would remain constant, the molar substitution[11]) (MS) would be greater than one.

Several methods exist for polymerizing alkylene oxides[12,13]. The chain extension reaction of HPL with PO and KOH has been assisted by 18-crown-6 ether catalyst[14]. CEHPLs have been separated from the PO homopolymer by a series of liquid/liquid extractions[14].

This study was (a) to relate CEHPL composition to the chemical, molecular and thermal properties of the copolymer; and (b) to examine the influence of differences in the chemistry of the parent lignins on CEHPL properties.

EXPERIMENTAL

Three HPL preparations[2,3], based on lignins isolated from the organosolv and the kraft pulping process, were reacted with PO and isolated as follows:

Synthesis

HPL (11.0 g or 0.04 moles), KOH (0.58 g or 0.01 moles), 18-crown-6 ether (1.3 g or 0.005 moles), toluene (70 mL), and acetone (3.0 mL) were sealed in a 600 mL stainless steel stirred (Parr) reactor and heated to 75°C. PO was added through a syringe pump at a rate of 1.5 mL/hr until the desired level of chain-extension was achieved.

Isolation

The reaction product was isolated by evaporation of solvent and dissolution in acetonitrile[8]. Liquid/liquid extraction with hexane was used to remove PO homopolymer (PPO); and subsequent water/chloroform extraction removed water-solubles. The chloroform-solubles were brown CEHPL products which varied in consistency between a tacky solid and low viscosity liquid.

Analysis

Gel permeation chromatography (GPC) was performed on a set of 3 μ-spherogel columns (Altex) with gel sizes of 1,000, 10,000, and 100,000 Å using non-stabilized THF. Calibration was based on monodisperse polystyrene and lignin model compounds with molecular weights up to 784 g/mol[15]. Flow rate was 1 mL/min and detection was by UV (280 nm).

The ^{1}H-NMR spectra were obtained for acetylated CEHPLs on a Bruker 270 MHz instrument using deuterochloroform as solvent and TMS as internal standard. Quantitative analysis was performed as described elsewhere[8].

Ultraviolet (UV) absorbances were determined on a Varian-Cary 219 spectrophotometer at 280 nm[16]. Total hydroxyl content was determined by back titration of acetic acid after acetylation of the CEHPLs[17].

Glass transition temperatures (T_gs) were determined using a Perkin-Elmer Differential Scanning Calorimeter Model-4, equipped with a Thermal Analysis Data Station (TADS). About 20 mg of sample was heated to 120°C, cooled to -80°C, and scanned at 20°C/min with dry helium as purge gas. The T_g was defined as one-half the change in heat capacity occurring over the transition.

RESULTS AND DISCUSSION

Chemical Analysis

The composition of CEHPL copolymers was investigated by ^{1}H-NMR and UV (280 nm) spectroscopy, and by total hydroxyl determination. ^{1}H-NMR analysis employed acetylated CEHPLs in accordance with earlier work[8]. Differences between the ^{1}H-NMR spectra of lignin, HPL, and CEHPL (Table 1 and Figure 1) indicated an increase in hydroxypropyl character by exhibiting greater signal intensity in ranges 4/5 and 8 with rising

TABLE 1

Chemical Analysis of Chain-Extended Hydroxypropyl Lignins (CEPHLs)

CEHPL Type	^{1}H-NMR Signal in Range (% total) 2&3	4&5	6&7	8	Molar Substitution (MS) Method[1] A	Method[1] B	Ave.
OS-HPL	11.1	38.0	23.7	27.1	1.0	-	1.0
OS-A	9.9	38.8	20.7	30.6	1.5	-	1.5
OS-B	6.4	43.1	13.2	36.8	2.8	3.1	3.0
OS-C	2.1	45.1	10.5	42.3	4.1	4.9	4.5
OS-D	1.6	45.2	7.0	46.2	6.6	7.8	7.2
KL(I)-HPL	10.4	38.6	23.8	27.2	1.0	-	1.0
KL(I)-A	8.7	40.5	16.3	34.6	2.1	2.2	2.2
KL(I)-B	6.0	41.2	12.9	39.9	3.1	3.2	3.2
KL(I)-C	4.9	44.4	11.7	39.0	3.3	3.9	3.6
KL(I)-D	4.5	45.4	10.1	40.4	4.0	4.4	4.2
KL(I)-E	4.5	43.2	9.5	42.8	4.5	4.7	4.6
KL(I)-F	2.4	46.3	7.0	44.3	6.3	7.2	6.8
KL(II)-HPL	12.2	36.7	24.9	26.2	1.0	-	1.0
KL(II)-A	6.5	36.0	21.2	36.3	1.7	2.1	1.9
KL(II)-B	4.0	42.5	15.4	38.1	2.5	3.3	2.9
KL(II)-C	2.9	44.4	8.4	44.3	5.3	6.1	5.7

[1] Defined in text.

amount of PO added to the reaction. The signal in range 2/3 decreases concomittantly. These signals are due, in part, to the methylene (range 5), methine (range 4) and methyl protons (range 8) on PO, and the aromatic protons (ranges 2/3) in lignin, respectively.

The MS can be calculated from ^{1}H-NMR data in two ways (Table 1). The first method (method A) was adopted from earlier work[8] and it is based on the ratio of the ^{1}H-NMR signals representing

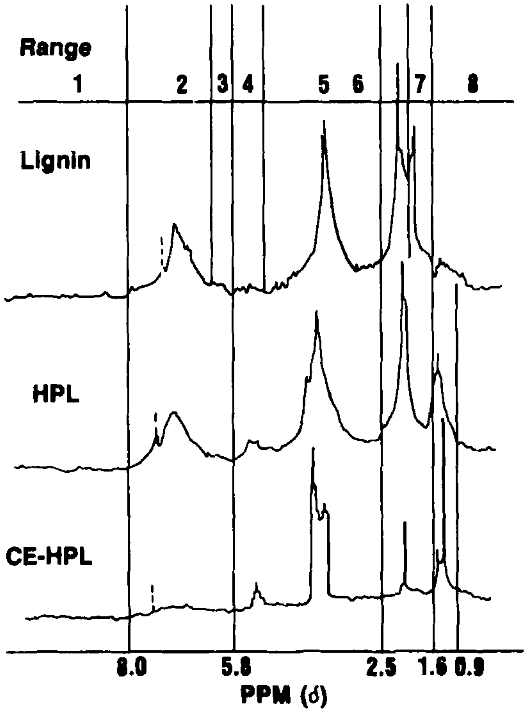

FIGURE 1. ^{1}H-NMR spectra of a lignin, hydroxypropyl lignin (HPL) and chain-extended hydroxypropyl lignin (CEHPL). The ranges were adopted from reference 8.

the methyl group of the propyl substituent (range 8) and that of the acetyl group (range 6/7). The second method (Method B) is based on a distinction between CH_3 signals in relation to the type of bonding, and this was only applicable to the more highly substituted CEHPLs. For these spectra one could distinguish two doublets in range 8 (representing the CH_3 group). The downfield doublet can be assigned to the protons of the methyl group of the PO unit connected to the aromatic oxygen, while the upfield

TABLE 2

Composition of CEHPLs

CEHPL Type	Ave. MS	Lignin Content of CEHPL (%)[1]	HPL Content of CEHPL (%)[2]	OH Content of CEHPL (%)	
				^{1}H-NMR	Titration
OS-HPL	1.0	67	100	9.8	6.8
OS-A	1.5	58	86	8.4	5.1
OS-B	3.0	41	61	6.3	3.4
OS-C	4.5	32	47	4.9	2.8
OS-D	7.2	22	33	3.5	1.7
KL(I)-HPL	1.0	65	100	11.4	7.2
KL(I)-A	2.2	45	70	7.5	4.9
KL(I)-B	3.2	36	56	5.6	3.9
KL(I)-C	3.6	34	52	5.0	3.5
KL(I)-D	4.2	30	47	4.9	2.4
KL(I)-E	4.6	28	44	4.6	2.1
KL(I)-F	6.8	21	33	3.6	1.8
KL(II)-HPL	1.0	63	100	10.4	6.7
KL(II)-A	1.9	48	75	7.2	4.4
KL(II)-B	2.9	37	59	5.4	2.8
KL(II)-C	5.7	23	37	4.0	1.9

[1] Determined from:

$$\frac{(58 * DS) + 180}{[(MS * 58) * DS] + 180} * 100$$

whereby the degree of substitution (DS) was taken as 80% of the values given in ref. 8.

[2] Determined from:

$$\frac{180}{[(MS * 58) * DS] + 180} * 100$$

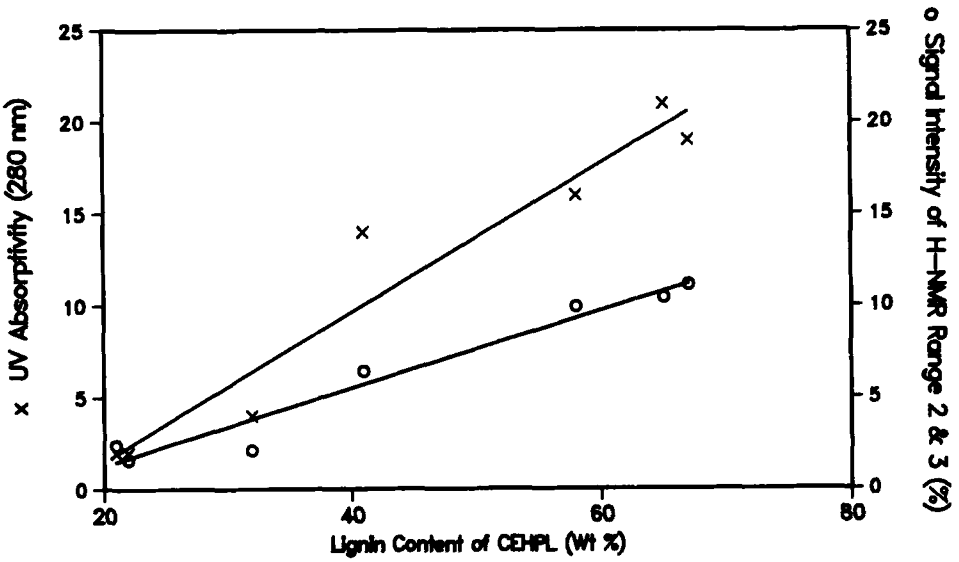

FIGURE 2. Relationship between the intensity of the ^{1}H-NMR aromatic signal, range 2&3, (O), the UV absorptivity at 280 nm (X) and the lignin content of the CEHPLs.

doublet was assigned to the methyl protons of subsequent (PO-PO linked) PO units. This assignment was based on the downfield shift induced by the high electron density surrounding the aromatic ring[18]. By ratioing these doublets it was possible to estimate the MS of a CEHPL. Table 1 illustrates fair agreement between the two methods.

Lignin (or HPL) content of the CEHPL can be computed on the basis of both the degree of substitution (DS) and the MS of the copolymers (s. Table 2). The data in Table 2 show that lignin content decreases steadily with increasing chain extension. Lignin content drops to ca. 20% when MS reaches about 7.

The UV absorption response of the CEHPL at 280 nm is specific for the aromatic repeat unit of lignin[16]. As the lignin content in the CEHPL decreases, the UV absorbance declines, Figure 2. A linear relationship indicates that the CEHPL composition varied in a consistent manner. Neither ^{1}H-NMR nor UV absorptivity revealed differences between chain-extended organosolv or kraft lignin. These lignins differ in their chemical structures but the differences are overwhelmed by the effects of chain extension.

Hydroxyl content was determined by ^{1}H-NMR and by titration (Table 2)[8,17]. The ^{1}H-NMR values are consistently higher than those obtained from titration. This difference was attributed to consistent errors with the calculated values for DS which assumed that the number of protons (per C_9-unit) on the HPLs and CEHPLs remained the same as that of the original lignin. This assumption is tenuous, and it is probably responsible for the observed systematic error.

Hydroxyl contents determined by both titration and ^{1}H-NMR (Figure 3) are compared with theoretical hydroxyl content of a hypothetical lignin hexamer. The theoretical curve was calculated assuming a DS of 1.5 and a C_9-unit weight of 180. Both of the measured hydroxyl contents follow the shape of the predicted curve. This systematic decrease in the hydroxyl content was consistent with an increase in the MS of the CEHPL.

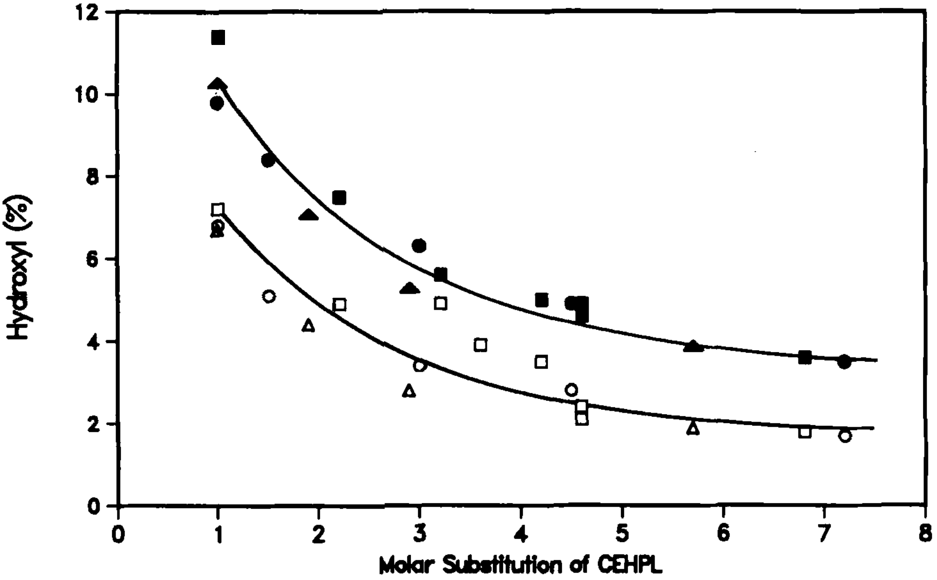

FIGURE 3. Total hydroxyl content as measured by ^{1}H-NMR (filled symbols) and titration (open symbols) of CEHPLs; OS (○), KL(I) (□) and KL(II) (△). The line represents the OH content of a theoretical hexamer with a DS of 1.5

Molecular Weight Analysis

High performance gel permeation chromatography was used to characterize the CEHPLs in regard to their molecular structure[19]. The results (Figure 4 and Table 3) in terms of number and weight average molecular weights, $\bar{M}_n$ and $\bar{M}_w$, respectively, as well as dispersity ratio (DR) and first moment of $\bar{M}_n$ (S_n) indicate that as MS increases, the molecular weight increases. DR and S_n also increase. The predicted changes in $\bar{M}_n$ at a DS of 1.5, along with the actual $\bar{M}_n$ values (Figure 5) demonstrate that while an actual increase in $\bar{M}_n$ was expected,

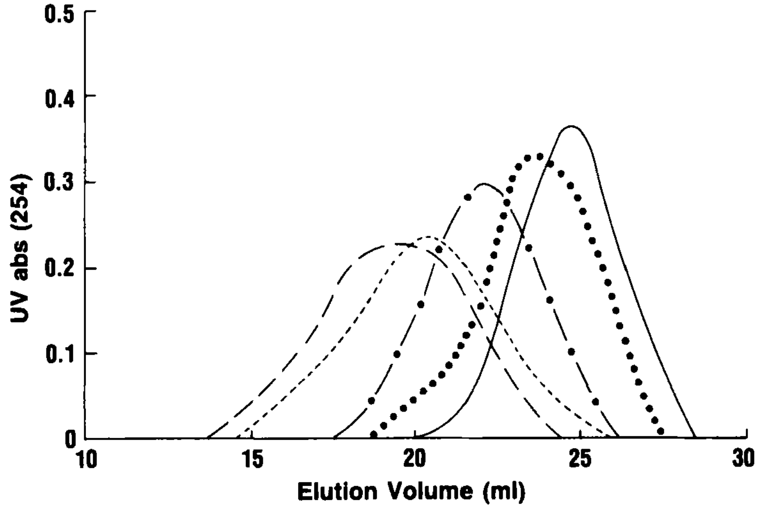

FIGURE 4. High pressure gel-permeation chromatograms of the organosolv series of chain-extended hydroxypropyl lignins: OS-HPL (——), OS-A (···), OS-B (—·—), OS-C (x x), and OS-D) (- - -).

the experimental $\overline{M}_n$ of all CEHPL's was consistently larger than that predicted on the basis of mass gain by derivatization. This discrepancy may be explained with either a change in solubility of the copolymer molecules leading to an anomalous increase in hydrodynamic volume in relation to chain extension, or with some sort of association[20]. The observation that derivatization (by acetylation or silylation) may increase the average molecular weight of lignin by more than can be expected on grounds of functionality has been reported earlier[21], and was attributed to a change in hydrodynamic volume. This resulted in the recommendation[21] that unmodified lignins (or molecules with

TABLE 3
Molecular Weight and Thermal Properties of CEHPLs

CEHPL Type	Lignin Content of CEHPL (%)	$\bar{M}_n$ (*10^{-3})	$\bar{M}_w$ (*10^{-3})	DR[1]	S_n (*10^{-3})	T_g (C)	T_g Range (C)
OS-HPL	67	0.6	1.2	1.9	0.8	32	46
OS-A	58	1.3	2.4	1.9	1.6	5	48
OS-B	41	1.4	3.5	2.4	2.7	-14	40
OS-C	32	4.7	21.9	4.7	19.4	-50	21
OS-D	22	8.0	104.6	13.1	100.5	-54	8
KL(I)-HP	65	0.7	1.4	2.0	1.0	58	47
KL(I)-A	45	1.2	2.3	2.0	1.6	3	33
KL(I)-B	36	2.1	4.7	2.2	3.5	-20	26
KL(I)-C	34	6.8	18.0	2.7	14.2	-30	28
KL(I)-D	30	4.7	34.8	7.4	32.4	-36	21
KL(I)-E	28	8.5	77.0	9.1	72.6	-56	18
KL(I)-F	21	11.8	110.2	9.4	104.1	-65	16
KL(II)-HPL	63	1.0	1.7	1.7	1.1	63	40
KL(II)-A	48	1.2	2.7	2.2	2.0	25	32
KL(II)-B	37	1.9	6.3	3.3	1.9	-24	22
KL(II)-C	23	6.6	57.4	8.8	54.0	-53	18

[1] The ratio of $\bar{M}_w/\bar{M}_n$.

low MS) should not be calibrated with the same standards as those chemically modified (or with high MS); and average molecular weights of lignin cannot be calculated by subtracting the mass of the derivative groups from the average molecular weight of derivatized samples[21]. Thus, while the absolute values of the average molecular weights must be questioned, the trends and relative differences were considered to be reliable. No consistent differences in molecular weight for lignins from different sources were seen.

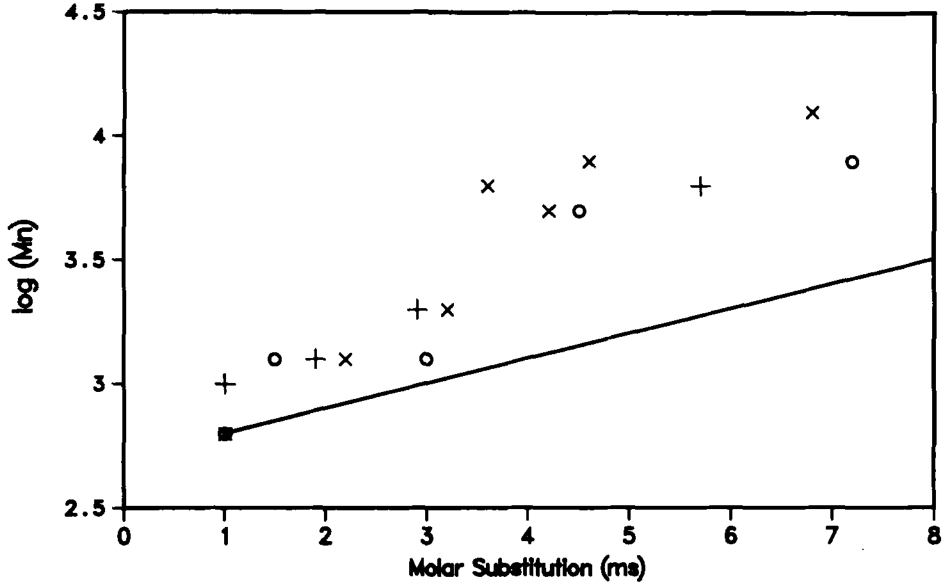

FIGURE 5. Changes in the molecular weight ($\overline{M}_n$) of CEHPLs, as measured from GPC, with increasing MS, measured by ^{1}H-NMR; OS (O), KL(I) (X) and KL(II) (+). The solid line represents the predicted $\overline{M}_n$ for a sample with 1.5 reactive sites on each lignin repeat unit.

Thermal Properties

The T_g and T_g range of CEHPLs were determined by DSC. T_gs ranged from -65 C to 63 C, and T_g range varied between 16 C and 48 C depending on copolymer composition (Table 3). The wide range in T_gs was reflected in the physical appearance of the CEHPLs which varied between a tacky solid and a low-viscosity liquid.

The T_g range may be taken as an indication of the heterogeneity of the system[22]. In the case of PPO only three types of covalent bonds are present in the backbone, which provides for a limited number of energy absorbing features. However, lignin, with its structural complexity possesses a large number of conformations which differ in their rotational energies. Thus as the composition of CEHPL varies, the relative contribution of the different components to energy dissipation also varies. As the PPO content increases, the relatively few dissipative mechanisms in this component dominate, providing for the observed reduction in T_g range.

A variety of equations exist for correlating a copolymer's composition with its glass transition. These vary from a simple linear average to complex equations that include free volume effects and secondary chemical interactions[23]. One simple but useful copolymer equation is the Gordon-Taylor equation[24],

$$T_g = \frac{T_{g1} + (kT_{g2} - T_{g1})\, C_2}{1 - (1 - kC_2)}$$

where T_g is the glass transition temperature of CEHPL copolymer, T_{g1} and T_{g2} are glass transition temperatures of HPL and PPO, respectively, C_2 is the weight fraction of PPO, and k is a constant for the copolymer system. The constant (k) for the copolymer system was determined from the experimental data with a procedure described elsewhere[25]. The determined value of 0.25 was very close to that found by a least squares fit of k-values to the experimental data (0.24). The Gordon-Taylor equation predicts that the T_g of the CEHPL decreases, in a non-linear

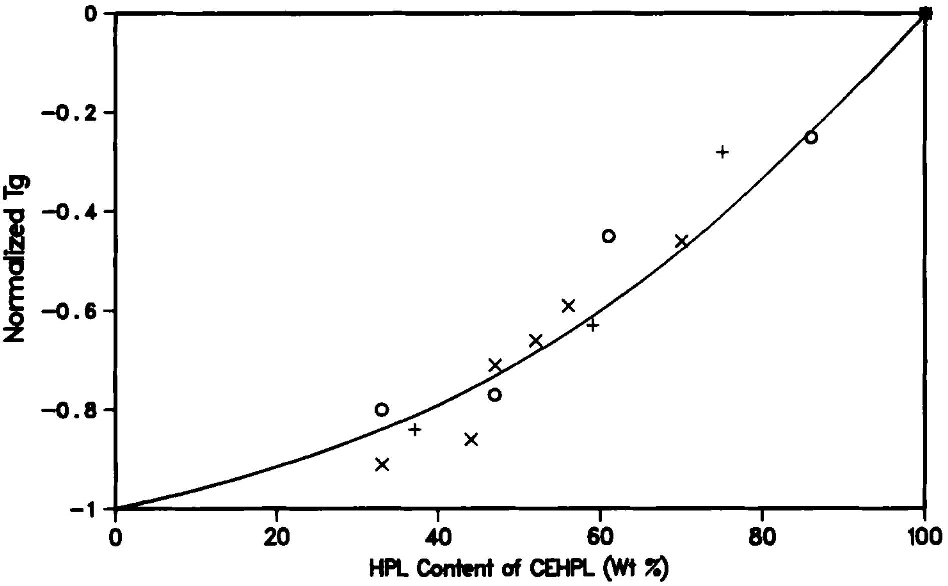

FIGURE 6. Changes in the normalized T_g with changes in the CEHPL copolymer composition. The solid line represents the T_g predicted from the Gordon-Taylor relationship (equation 3 in text) with k=.24. The normalization involves insertion of the T_g from either experiment or the Gordon-Taylor equation into the following equation. Normalized $T_g = (T_g - T_{g1})/(T_{g2} - T_{g1})$; where T_{g1} is between 32 and 63 C for the three respective HPLs, and T_{g2} is -75 C for polypropylene oxide homopolymer.

fashion, as the weight fraction of the low T_g-PPO increases. Normalized T_g values versus HPL content (Figure 6) are in good agreement with the normalized line predicted from the Gordon-Taylor equation. The normalization was used to alleviate differences in the T_g of the different HPL starting materials. Thus the effect of changes in composition (i.e., MS) could be shown for all of CEHPLs. (Parent lignin does not follow this model, and cannot be considered as the homopolymer since the hydroxypropylation reaction converts phenolic hydroxyls and carboxyls to secondary hydroxyls. The more acidic phenolic hydroxyls have a profound effect on T_g due to hydrogen bonding.) Defining HPL as the homopolymer produced agreement between the data and the Gordon Taylor model. This agreement is another example of how lignin behaves like a normal polymer, and allows prediction of material properties.

CONCLUSIONS

Hydroxypropyl lignins (HPLs) could be reacted with propylene oxide to produce lignin based copolymers. The chemical, molecular weight and thermal properties of these chain-extended hydroxypropyl lignin (CEHPL) copolymers could be related to their composition.

Quantitative analysis by H-NMR-spectroscopy revealed a continuous decrease in lignin signals (i.e., aromatic protons) and an increase in the intensity of methyl and methylene protons associated with the attached hydroxypropyl units. A similar decrease in UV absorptivity confirmed the decrease in lignin content as the molar substitution (MS) of the CEHPL increased. Both of these results indicate that the lignin content of the CEHPL copolymer decreased as the length of the hydroxypropyl chains increased. The hydroxyl content also decreased with rising MS. The total hydroxyl content could be determined by H-NMR and titration, with titration judged to be more reliable.

Gel permeation chromatographic analysis allowed for determination of the effects of MS on the molecular weight of the CEHPL. The molecular weight of the CEHPL increased with increasing MS. However, this apparent molecular weight increase was larger than predicted and the unexpected increase was attributed to an increase in the hydrodynamic volume of the CEHPL with MS.

The glass transition temperature (T_g) of the CEHPLs were found to be closely related to copolymer composition. The T_g of the copolymer decreased as the percentage of low T_g polyether component increased. This relationship followed the Gordon-Taylor model.

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