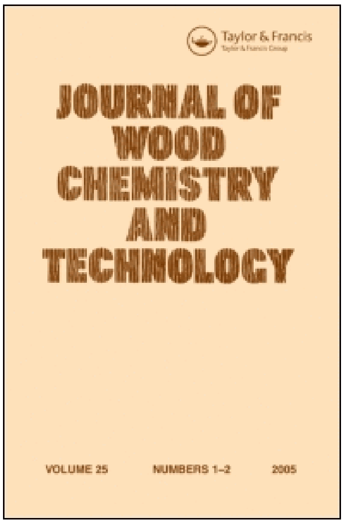


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Engineering Plastics from Lignin. 21.[1]Synthesis and Properties of Epoxidized Lignin-Poly (Propylene Oxide) Copolymers

Klaus Hofmann[a]; Wolfgang G. Glasser[a]
[a] Department of Wood Science and Forest Products, and Biobased Materials Center, Virginia, Tech Blacksburg, Virginia

To cite this Article Hofmann, Klaus and Glasser, Wolfgang G.(1993) 'Engineering Plastics from Lignin. 21.[1]Synthesis and Properties of Epoxidized Lignin-Poly (Propylene Oxide) Copolymers', Journal of Wood Chemistry and Technology, 13: 1, 73 — 95
To link to this Article: DOI: 10.1080/02773819308020508
URL: http://dx.doi.org/10.1080/02773819308020508

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 13(1), 73-95 (1993)

ENGINEERING PLASTICS FROM LIGNIN. 21.[1] SYNTHESIS AND PROPERTIES OF EPOXIDIZED LIGNIN-POLY(PROPYLENE OXIDE) COPOLYMERS

Klaus Hofmann and Wolfgang G. Glasser[2]
Department of Wood Science and Forest Products, and
Biobased Materials Center,
Virginia Tech
Blacksburg, Virginia

Dedicated to the memory of Kyosti V. Sarkanen

ABSTRACT

Epoxy resins were prepared from hydroxyalkyl lignin derivatives with varying degrees of alkoxylation. The epoxy-functional copolymers were fractionated into narrow molecular weight, chemically uniform prepolymers with good solubility. The epoxy resins were cured with diamine, and the network polymers were characterized by mechanical testing. Modulus and ultimate strength increased with lignin content and ultimate strain decreasing. The resins were comparable or superior to diglycidyl ether of bis-phenol A (DGEBA)-based (control) resins in strength.

INTRODUCTION

Epoxy resins are widely used for diverse applications in adhesives, coatings, structural materials, appliances, matrices of composites, etc. Most epoxy resins are composed of low molecular weight aromatic precursors that can be crosslinked using an oxirane functionality. Suitably functionalized lignin represents an alternative precursor that combines the benefits of renewability and biodegradability, at least as far as the parent source is concerned[3,4]. Especially its polyfunctionality and brittle, glassy (rigid) nature appear to be of certain usefulness for the development of thermosetting resins[5,6] such as polyphenolics[5,7,8], polyurethanes[9-12], polyacrylics[13], and epoxides[14-24]. Several approaches have been taken to incorporate lignin or lignin derivatives into epoxy resins with the aim of partially replacing oil-based materials and to find a cost-effective utilization for lignin.

The fact that lignin may be soluble in commercial epoxy resins has been employed for the purpose of adding lignin to uncured resins as filler or extender[22,23]. The functionalization of lignin with glycidyl ether groups by reaction with epichlorohydrin (in aqueous alkali) has been the basis for the synthesis of crosslinkable (with diamines or anhydrides) epoxy-functional lignin derivatives[14-21]. This approach has been taken with water-insoluble lignins[14-20] as well as water-soluble ligninsulfonates[21]. Carboxy group-enriched lignin derivatives, from the treatment of lignin with ozone, have also been used as oligomeric crosslinking agents for epoxy resins[24]. Among the many options for adding lignin to epoxy resins, glycidylation provides the best assurance for covalent incorporation of lignin into the network structure of the cured resin[6].

When epoxidizing lignin, one has to overcome problems intrinsic to lignin. Not only are many lignins insoluble in most organic solvents, they also bear a range of hydroxyl groups with non-uniform reactivity. Chemical modification can provide a remedy. It was the aim of this and earlier studies[18,19,25] to investigate the possibility of epoxidizing modified lignins, with superior solubility characteristics and with uniform reactivity, and to study their cure and network forming behavior (mechanical properties and morphology) as a function of compositional parameters. This report examines resin synthesis and mechanical properties of networks crosslinked with an aromatic diamine.

EXPERIMENTAL

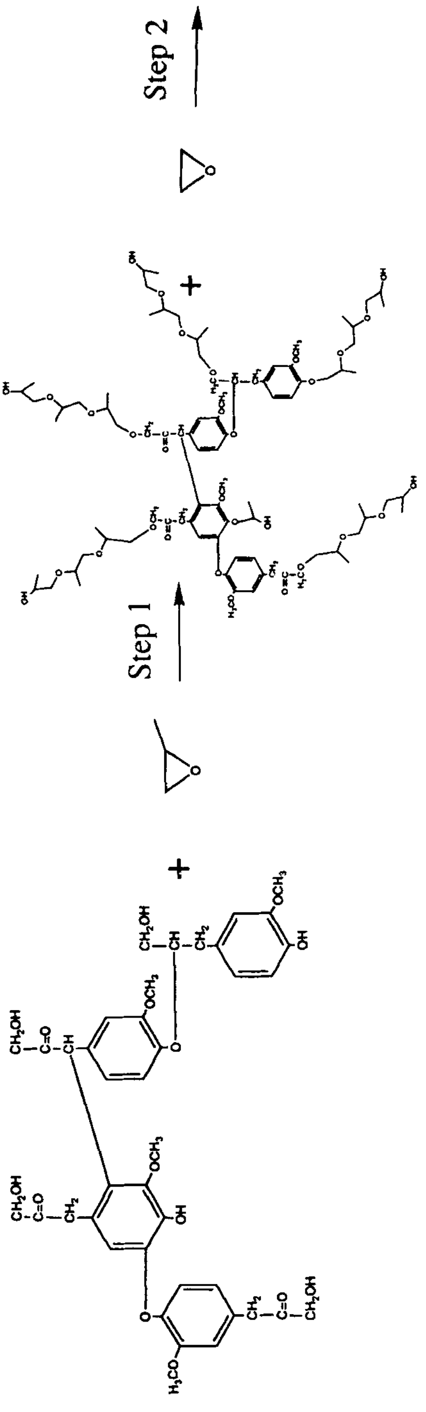
I. Materials:

The lignins used in this study were (a) alkali-extracted autohydrolysis lignin from steam exploded yellow poplar (Liriodendron tulipifera) wood[26], and (b) an organosolv lignin (Aldrich Chemical Company, #37,101-7) which was used as received.

II. Synthesis Methods:

All lignins were reacted with propylene oxide to improve their solubility. Degree of propoxylation varied. All derivatives were capped with ethylene oxide to convert secondary into primary hydroxyl groups. A typical hydroxyalkylation experiment (Fig. 1, steps 1 and 2) involved the following steps in accordance with Kelley et al.[27] and de Oliveira and Glasser[28]: Lignin with a moisture content of ca. 6% was dried in toluene by azeotropic distillation. The lignin toluene suspension was previously mixed with distilled water containing ca. 50% potassium hydroxide. Dry suspension of potassium lignate (550 g) in toluene was then added to a pressure reactor which was sealed. The temperature was raised to 140°C under constant vigorous stirring. Propylene (PO) and ethylene oxide (EO) were then added sequentially and in small portions to the pressurized reactor. After an initial injection of PO, the temperature was lowered to 110°C. This was found to minimize the formation of alkylene oxide homopolymer[29]. After completion of the reaction and cooling, the reactor was opened and the product collected. Depending on the extent of modification, the reaction products were either in solution (medium to highly modified), or they precipitated upon cooling from the toluene solution (short chain-extension). Toluene was distilled off under vacuum.

Seven samples were prepared by this method. All products were soluble in most common organic solvents (acetone, methylene chloride, chloroform, acetonitrile, etc.). The samples were designated with the prefix LX followed by four digits denoting the number of moles of PO (first 2 digits) and the number of moles of EO (last 2 digits) per kg of dry lignin according to Table 1. Hydroxyalkylation was followed by epoxidation of the copolymer with epichlorohydrin (Fig. 1, step 3). The lignin polyols were thereby converted into soluble, oxirane-bearing star-like copolymers with rigid polyphenolic cores and flexible polyether arms. A typical epoxidation


Step 1
Step 2

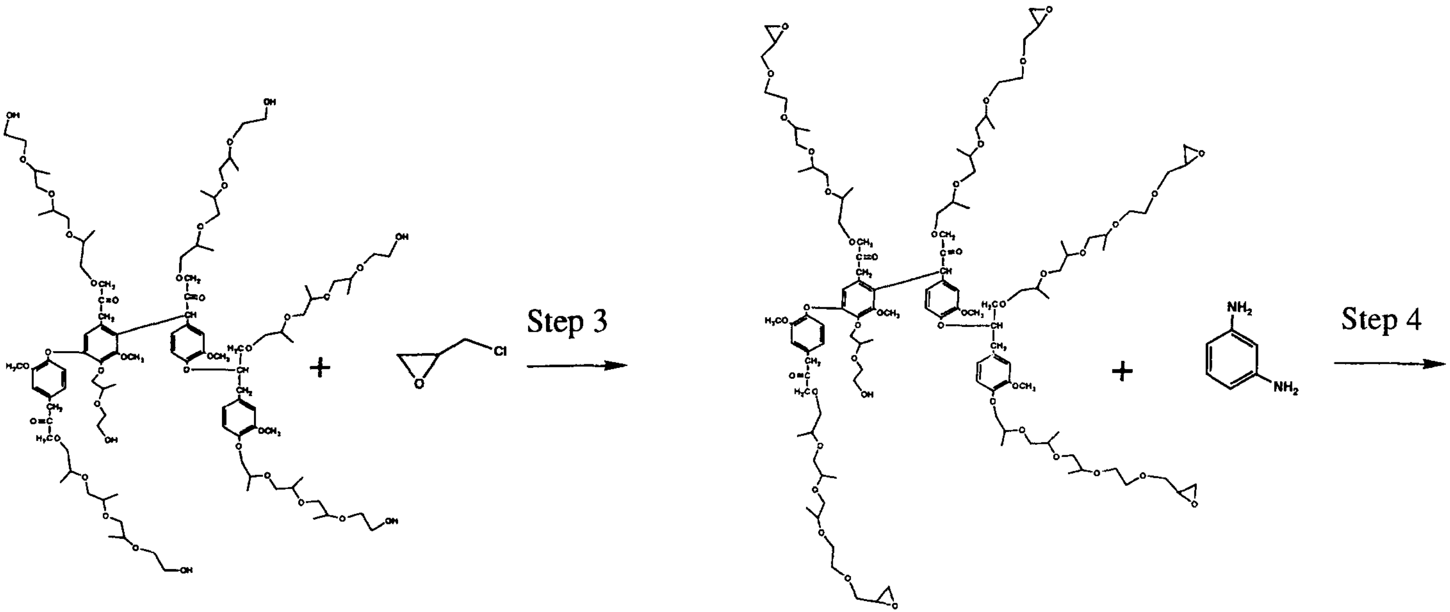


Figure 1. Schematic Lignin Modification and Crosslinking Protocol. The Scheme Illustrates Propoxylation (Step 1); Ethoxylation (Step 2); Glycidylation (Step 3); and Crosslinking (with mPDA) (Step 4) of an Epoxy Resin Based on the Conceptual Hardwood Organosolv Lignin Structure Used Prviously for Illustration Purposes (26).

(continued)

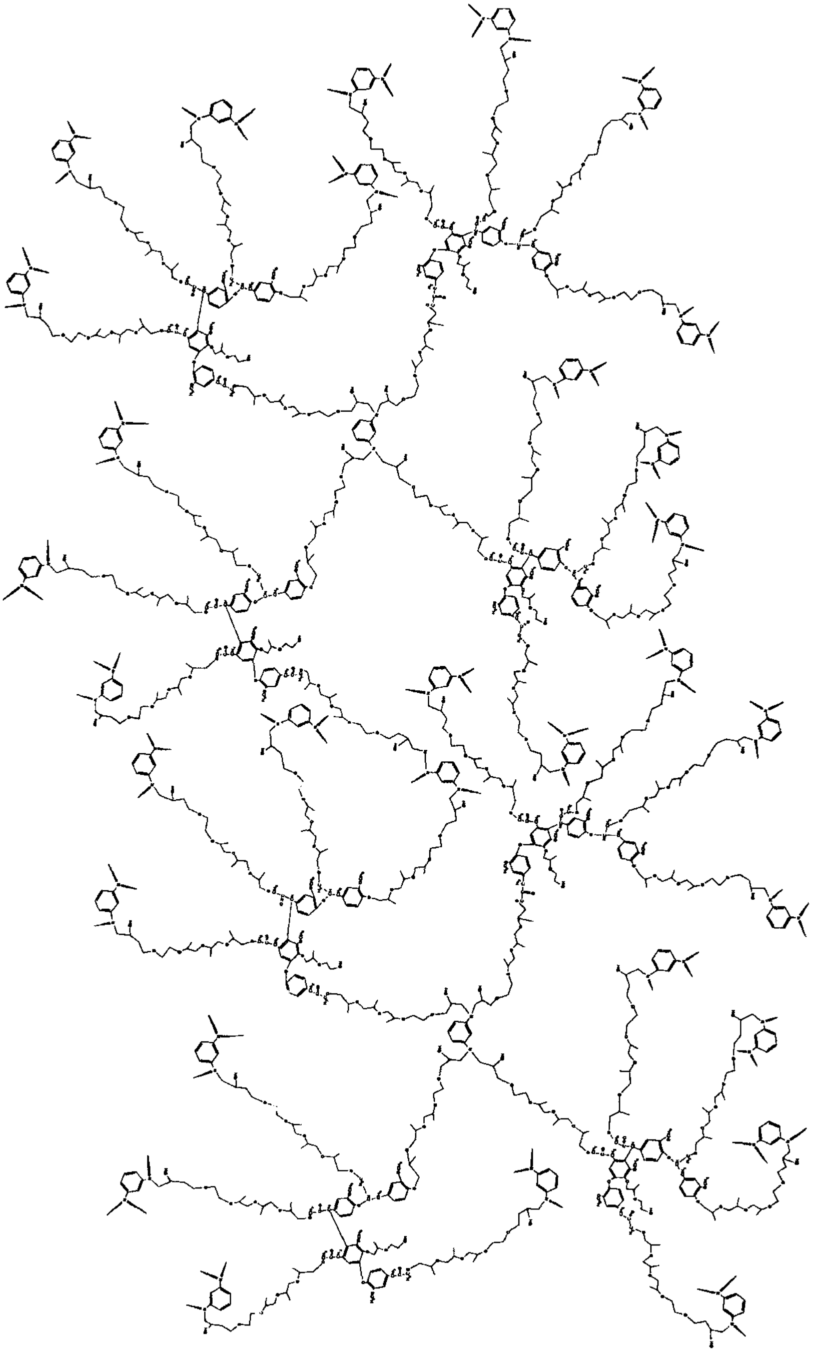


Figure 1. Continued

TABLE 1
Hydroxyalkyl Lignin Preparations

Lignin Type	Designation[2]	Moles of AO[3]/kg Lignin	
		PO	EO
Organosolv, unfractionated[1]	LX0013	0	13
Steam-explosion, unfractionated[1]	LX0513	5	13
"	LX3010	30	10
Steam-explosion, fractionated[1]	LX1204	12	4
"	LX1512	15	12
"	LX2404	24	4
"	LX4003	40	3

[1] Fractionation refers to separation of components according to chemical (homo- vs. copolymer) and molecular (molecular size) parameters (see Figures 2 and 3).

[2] First two digits refer to the amount of PO used (in moles/kg lignin); and the last two digits specify the amount of EO used.

[3] AO stands for alkylene oxide (representing propylene as well as ethylene oxide, PO and EO, respectively).

protocol involved the following steps in accordance with Nieh and Glasser[18,19]: A 25% solution of hydroxyalkyl lignin in toluene was reacted with 10 moles of epichlorohydrin per OH-equivalent. Finely ground KOH was added in four equal portions of one equivalent each per available copolymer hydroxy equivalents, in 24 hour intervals. After 120 hrs the reaction was quenched by the addition of solid carbon dioxide. The solution was centrifuged twice at 5,000 rpm for 20 minutes to remove undissolved KCl and K_2CO_3. Solvent-free product was filled into polyethylene jars and stored at -20°C. Before curing, the resins were fractionated by solvent precipitation which removed the inevitably formed poly(propylene oxide) homopolymer (Figure 2), and which produced fractions with narrower molecular weight distribution than the original copolymer and with varying lignin content (Figure 3). This involved (Figure 4) a two-step treatment designed to first remove soluble,

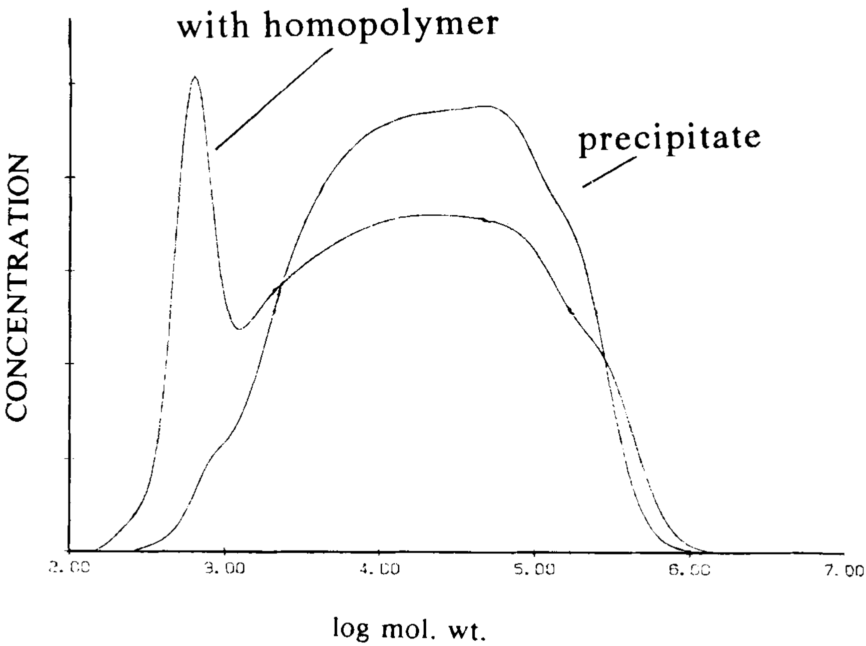


Figure 2. Molecular Weight Distributions of Unfractionated and Fractionated Lignin Derivative.

homopolymer-rich polyol of low molecular weight (LX1204A0) from copolymer (LX1204A), and subsequently (following re-dissolution of precipitated copolymer in acetone) fractionating copolymer according to molecular weight. The latter part of the fractionation procedure involved the stepwise addition of hexane to a 10% concentrated solution of lignin derivative in the combined total proportion of 10:1 (v/v, hexane/acetone) (Figure 4). Stepwise collection of hexane insolubles produced fractions which differed in both molecular weight and copolymer composition. Large, star-like copolymer molecules having high lignin content precipitated first (see Figure 4) followed by progressively smaller components as hexane concentration increased. The fractionated lignins were crosslinked with meta-phenylene diamine (m-PDA), and the crosslinked materials were tested for

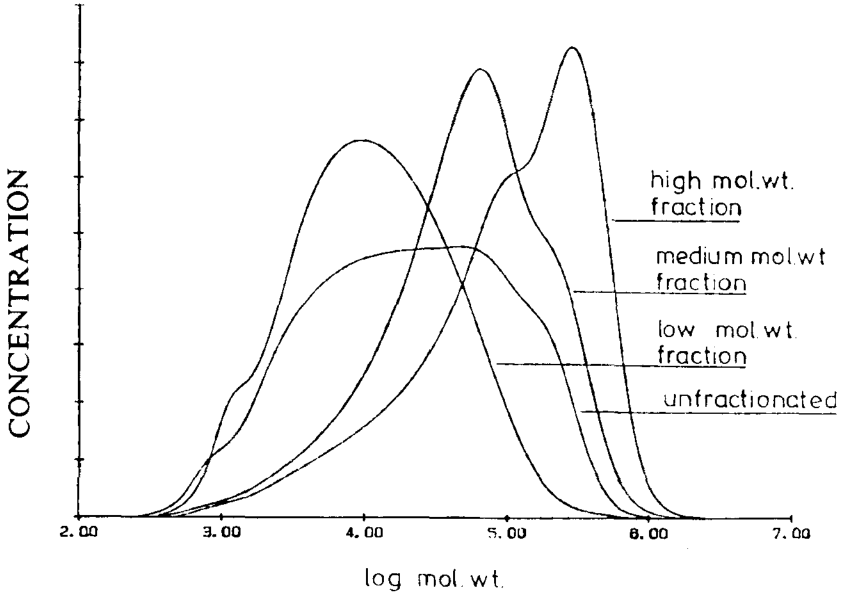


Figure 3. Molecular Weight Distributions of Lignin Derivative LX4003 Fractionated According to Molecular Weight.

mechanical performance. A typical crosslinking protocol involved the following steps: A stoichiometric amount of m-PDA in THF solution (ca. 20% w/v) was added to a lignin epoxy solution in methylene chloride (ca. 20% w/v) and poured into aluminum foil-covered Teflon® dishes. They were left in the hood until the solvent had evaporated (ca. 24 hours). The uncured mixtures were then transferred to a desiccator and dried under vacuum at room temperature for another 24 hrs. They were subsequently stored at -20°C. Five dogbone specimens were dye-cut with a Brockton Cutting Dye (Model D-638-5) for each sample. Samples LX1204A1, LX2404A1, LX0013 and EPON 826 (control) were prepared by casting the liquid resin without the aid of solvent into dogbone shaped, silicon rubber molds. When needed, the uncured resin samples were cured in a vacuum oven at 140°C.

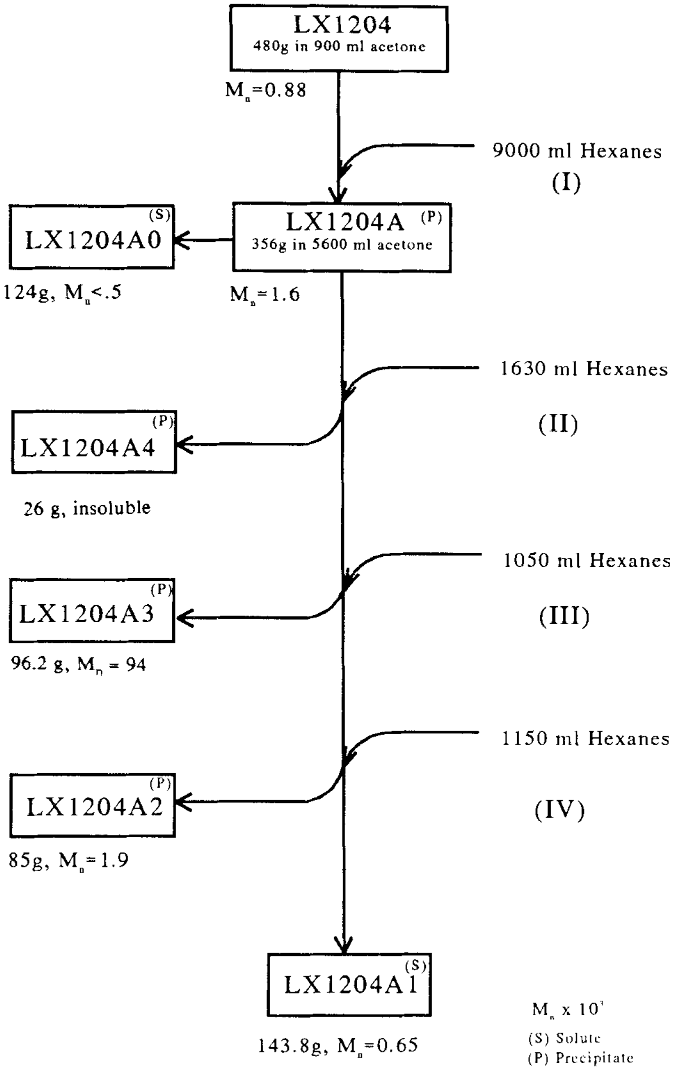


Figure 4. Epoxy Fractionation Protocol.

III. Analysis Methods:

1. Epoxy Content: The determination of the epoxy equivalent weight was carried out by potentiometric titration of the epoxide solution (chloroform) with hydrogen bromide[30]. A 0.05 N HBr solution in acetic acid was prepared and routinely checked by titrating a known quantity of potassium bi-phthalate. The change in resistivity was recorded on a Brinkman E576 Potentiograph.

2. Molecular Weight Distributions (MWD): MWD's were recorded by gel permeation chromatography with a refractive index (Waters 410) and a differential viscometry (Viscotek Model 100) detector connected in series with three-spherogel columns (Waters Associates) of size 10^3 Å, 10^4 Å, and 10^6 Å. The mobile phase was THF. Molecular weight calculations were performed by UNICAL™ software on an IBM compatible computer. This method has previously been applied to the measurement of molecular weights of hydroxypropyl lignins (HPL) by Siochi et al.[31].

3. Lignin Content and Alkylether Chain Length: Lignin content was quantitatively assessed by UV absorptivity measurements in accordance with the procedure of de Oliveira and Glasser[28].

4. Mechanical Tests: The dogbone-shaped samples, either as dye-cut or mold-cast specimens were tested on a miniature stress-strain materials tester ("Minimat") manufactured by Polymer Laboratories. Measurements were carried out at room temperature, and the rate of deformation was 0.25 mm/min. Load and deformation data were transmitted to a personal computer and could be redrawn as stress vs. strain, load vs. deformation, and modulus vs. strain curves.

RESULTS AND DISCUSSION

1. Preparation of Lignin-Based Epoxides:

Compositional data of the lignin-polyether copolymer epoxides are compiled in Table 2. Epoxidation of the lignin-poly(alkylene oxide) copolymers with excess epichlorohydrin and with stepwise addition of potassium hydroxide[18,19] is an efficient procedure for preparing lignin-

TABLE 2
Molecular Weights, Copolymer Compositions, and Epoxy Contents of Lignin-Polyether Copolymer Epoxides

Sample	Homopolymer content	Fraction #	Fraction %	M_n x10^3	M_w x10^3	Lignin Content %	Epoxy Eq. Weight (EEW) g/eq	Functionality (M_n/EEW)	Ave. Arm Length
LX0013	n/a	n/a		1.2	9.9	57	670	2	288
LX0513	n/a	n/a		11.3	129.0	55[2]	532	21	239
LX1204	26	A1	41	0.65	3.0	16	231	4	195
		A2	24	1.9	28.0	37	399	5	252
		A3	27	93.8	213.7	42	439	200	254
		A4	7	Insoluble					
LX1512	17	A1	30	1.4	4.2	34	390	4	257
		A2	10	2.1	9.0	44	550	4	308
		A3	58	6.4	33.4	48	430	15	224
LX2404	38	A1	44	0.79	4.3	21	360	4	283
		A2	28	3.02	36.0	39	507	21	311
		A3	28	30.2	132.8	34	602	95	400
LX3010	n/a	n/a		3.6	32.3	25[1]	413	9	310
LX4003	26	A1	48	5.2	24.0	35	385	13	251
		A2	21	15.3	96.0	43	518	30	295
		A3	32	22.7	190.0	42	714	30	416

[1] Estimated from lignin propylene oxide feed ratio; unfractionated sample.

containing epoxy resins. Functionalized lignins had molecular weights ranging from 1,000 to 30,000 and epoxy equivalent weights (EEW) of 200 to 700 g/eq. Functionality, that is the average number of epoxy functional groups per (number) average molecular fragment, was between ca. 2 and 200.

During sample handling and functionalization, intermolecular side reactions could not be avoided completely. Although no gel formation was observed, the number of species with molecular weights of about 10^5 increased considerably at the expense of smaller molecules (Figure 5). The most obvious mechanism for this side reaction is the reaction of an oxyanion with a newly formed epoxy group. Experimental evidence (not shown) reveals that this rise in molecular weight is considerably less pronounced with the ethoxylated organosolv lignin (LX0013) than with the more highly propoxylated copolymer samples. This suggests that highly soluble, low molecular weight lignin derivatives with primary hydroxy functionality are best qualified for epoxidation.

In spite of the goal to eliminate homopolymer formation during propoxylation, the formation of homo-poly(propylene oxide) seemed unavoidable. Homopolymer content was generally around 20% except for very low degrees of modification. However, extraction with a 1:10 acetone:hexane solvent mixture essentially removed all homopolymer (see Figure 2). The further fractionation of the homopolymer-free copolymer in acetone-hexane systems of increasing hexane content had a two-fold effect. Firstly, reducing the "goodness" of the solvent (acetone) by addition of a nonsolvent (hexane) decreases the radius of gyration of the star-like copolymers and results in the eventual precipitation of the copolymer species in the order of decreasing molecular weight, thereby separating the highly polydisperse lignin epoxides into fractions of narrower MWD. Following the diagram of Figure 4, and the molecular weight values of Table 1 as well as the graphs of the MWD (Figures 4 and 5), it is evident that the fractionation method employed efficiently separates the epoxide molecules by molecular weight. Secondly, fractionation in acetone-hexane has also a separation effect

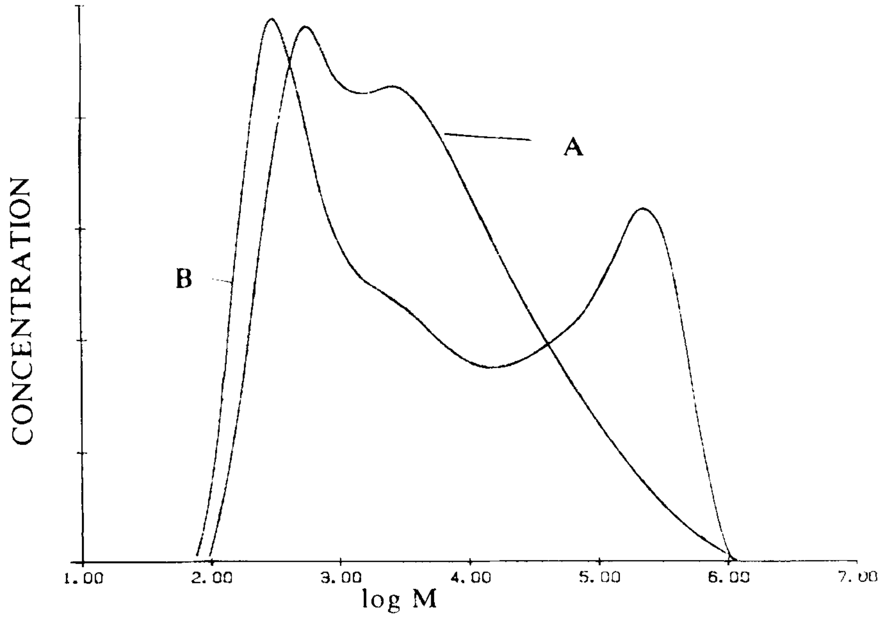


Figure 5. Molecular Weight Distribution of Lignin Derivatives Before (A) and After (B) Epoxidation with Epichlorohydrin.

in terms of lignin content. Hexane is a good solvent for poly(propylene oxide) but a non-solvent for lignin and the copolymer. Hence, those species with relatively higher aliphatic polyether content remain in solution longer once the hexane content increases. Indeed, the lignin content data (Table 2) reveal that an inverse relationship exists with hexane concentration. The fractions precipitating at the lowest hexane content have the highest lignin content. However, only for the short-chain modified lignins, i.e., LX1204 and LX1512, this trend is continuous while the more highly chain-extended samples (LX2404 and LX4003) exhibit a lignin content maximum for the medium fraction and a slight decrease for the first precipitate.

It is conceivable that the fractionation by lignin content has an influence on the length of the poly(propylene oxide) arms. Their size can be calculated from the lignin content and the epoxy functionality by assuming that all arms are capped by epoxy end-groups[32]. However, such calculations overestimate the length of the ether arms, especially for the high molecular weight fractions because those chains having participated in the premature inter-molecular crosslinking during epoxidation are not accounted for in the calculation of functionality. Nevertheless, the calculated sizes of the polyproylene oxide side chains permit the estimation of the overall length of the flexible connections in the cross-linked copolymers. The data of Table 2 suggest that the so-calculated arm lengths are remarkably invariable, between 200 and 300 daltons, or about 4-6 propylene oxide units in length. This suggests that all hydroxy groups were extended during the propoxylation reaction to the same extent regardless of the size of the lignin molecules (i.e., all OH-groups are equally accessible).

2. Mechanical Performance of Crosslinked Lignin-Based Epoxides:

The incorporation of lignin into chemical networks usually strives for a balance between optimum mechanical performance and maximum amount of lignin. Modification of lignin prior to network formation improves (resin) solubility and provides internal plasticization. Indeed, the results of the uniaxial tensile stress-strain tests (Table 3) reveal that the values of δ_{max} and E_{max} are in the order of, or surpass, the respective numbers of the DGEBA-based epoxy system (EPON 826). A general trend to stiffer and stronger materials can be observed with increasing lignin content, while simultaneously the ultimate extension decreases. The stiffest specimen came from a network which was made from unfractionated hydroxyethylated organosolv lignin, LX0013. With a strength of nearly 42 MPa and an elongation of 6%, this sample combines high stiffness with good strength at a lignin content of 57%. Of practical importance is that the organosolv lignin copolymer has low molecular weight ($M_n \sim 1{,}200$) which makes it a liquid at room temperature. Unlike liquid, low lignin-content fractions, however, this high lignin-content material can be cross-linked to become a glassy material with high T_g.

Stress-strain curves of several films prepared from LX1204 fractions are shown in Fig. 6. The high lignin content specimen LX1204A3 and the

TABLE 3
Tensile Strength and Modulus of Lignin-Polyether Copolymer Epoxy Networks

Sample	Prep.	σ_{max} (MPa)	ϵ_{max} (%)	E_{max} (MPa)	M_n of copolymer ($x10^3$)	Lignin Content (%)
LX1204A1	mold[1]	21.8	37	274	0.6	16
	film[2]	30.9	9.8	441		
LX1204A2	film	55.2	8.4	732	1.9	37
LX1204A3	film	56.9	6.1	917	93.8	42
LX2404A1	mold	4.5	16.2	77.8	0.8	21
LX2404A2	film	41.7	13.3	661	5.5	39
LX0013	mold	41.7	6.13	1012	1.2	57
DGEBA[3]	mold	31.5	6.2	499		

1) Lignin copolymer epoxides and crosslinking agent (mPDA) were mixed in neat form and cured in dogbone shaped silicon rubber mold.

2) Lignin copolymer epoxides and crosslinking agent (mPDA) were mixed in solution and film cast, test specimens were cut with dogbone shaped Brokton Cutting Dye (Model D-638-5).

3) EPON 826.

EPON 826 networks can be described as brittle failure types, while both, the medium and the low lignin-content films exhibit ductile failure behavior. However, the silicon rubber mold-cured sample LX1204A1 undergoes nearly cold drawing with a four-times greater elongation than its solution-cast and film-cured counterpart. The reasons for the differences are not immediately apparent.

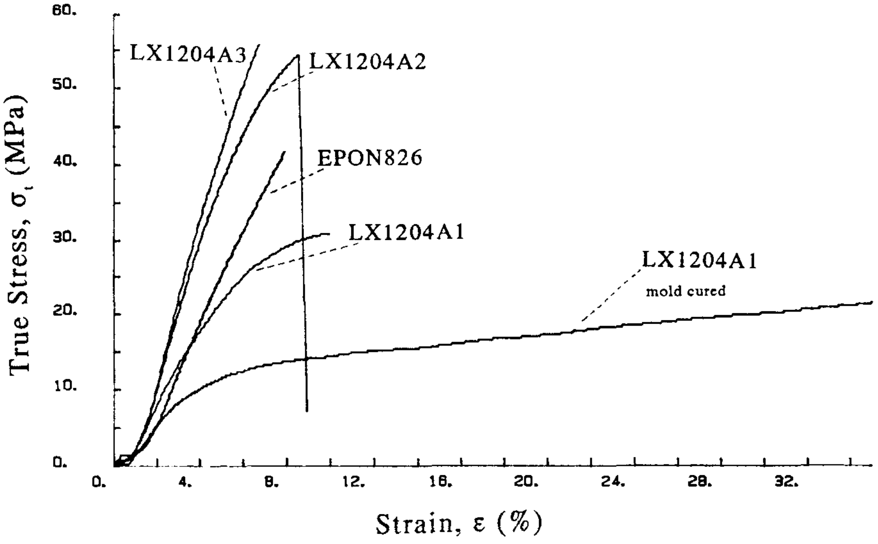


Figure 6. Stress-strain Curves of Cured Epoxy Resins.

An attempt was made to correlate the data to compositional parameters such as molecular weight and lignin content. A clear linear trend of increasing modulus with rising lignin content is noticeable (Fig. 7 a) which, extrapolated to 100% lignin, predicts an ultimate modulus of 1850 MPa. This is only slightly below the value of 2000 MPa reported by Falkehag for pure lignin[33]. This positive correlation between stiffness and lignin content, i.e, aromaticity, is expected and agrees with similar observations made by Kelley et al.[12] for lignin-containing polyurethane networks. Maximum strength also increases with lignin content (Fig. 7 b); however, a levelling-off beyond 40% seems evident. On the other hand, no systematic influence of molecular weight of the copolymers on mechanical data was detected.

CONCLUSIONS

Epoxidation of lignin-alkylene oxide copolymers which contain primary hydroxyl groups, by a method of adding 10-fold excess of epichlorohydrin to

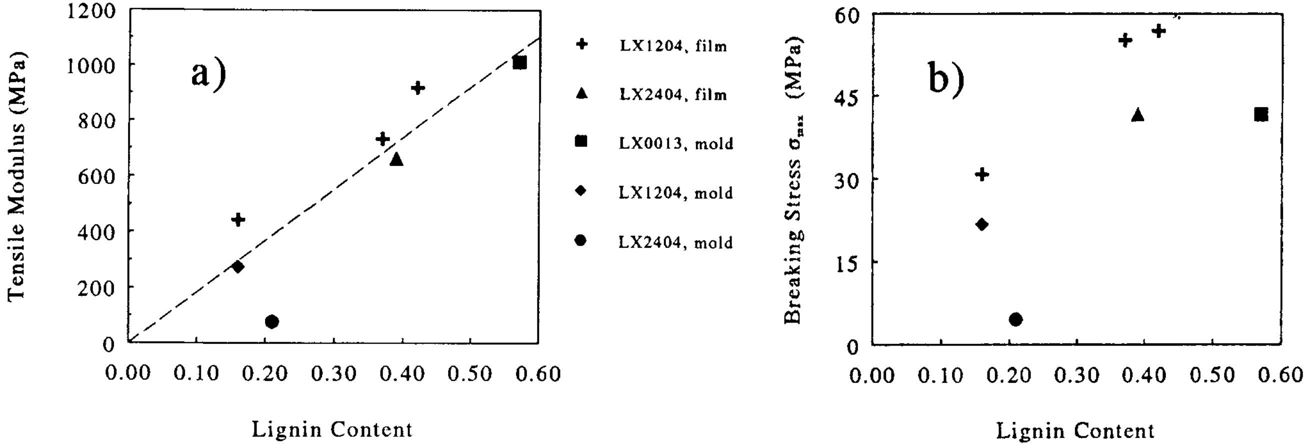


Figure 7. Tensile Modulus (a) and Breaking Strength (b) of Lignin-Based Epoxy Resins in Relation to Lignin Content.

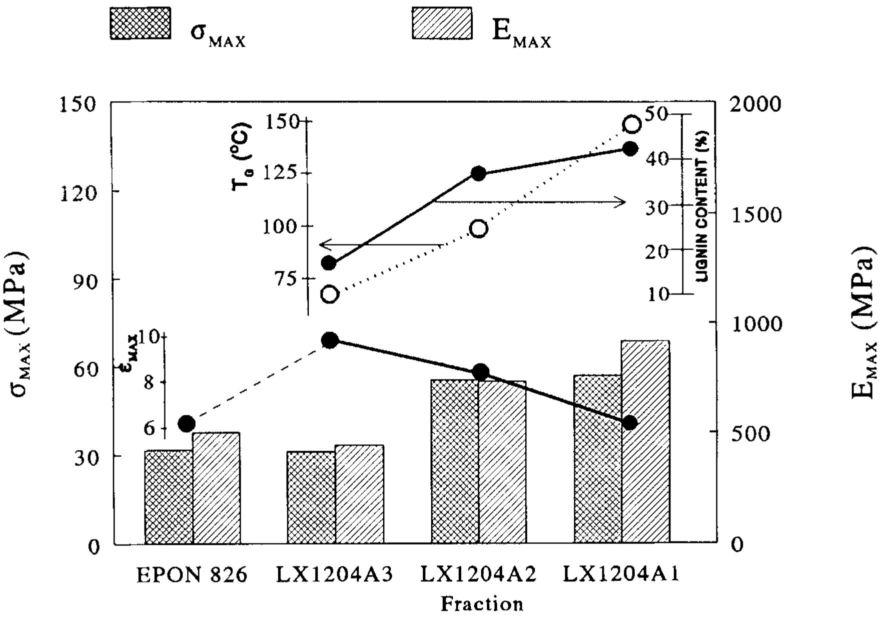


Figure 8. Mechanical and Thermal Characteristics of Three Lignin Epoxides and of EPON 826 (Control).

25% toluene (or methylene chloride) solutions and by the stepwise addition of KOH, has been carried out on eleven fractionated and unfractioned lignin derivatives with good conversion efficiency. The epoxide copolymers contain up to 57% lignin and are soluble in many organic solvents. Fractionation in acetone-hexane solutions has been shown to be an efficient method for extracting poly(propylene oxide) homopolymer and to yield fractions clearly separated by molecular weight and (to a lesser extent) by lignin content. The length of the epoxy group-carrying chain was nearly constant. Epoxy-amine networks which contain >50% lignin exhibit tensile strengths and moduli which are in the order of those of a commercial DGEBA-mPDA network. Independent of molecular weight of the prepolymers, a clear linear trend of modulus increase with lignin content was observed for all samples and fractions. Furthermore, maximum stress shows a positive trend with lignin content, while elongation at break usually declines.

A summary of these relationships as well as a comparison of the mechanical performance of the film-cured LX1204 fractions is given in Figure 8. δ_{max} and E_{max} of the three fractions are contrasted with the respective EPON 826 network. The change of δ_{max} is documented by the line graph above the bars. The inserted comparison of lignin content and glass transition temperature for the three fractions furthermore exemplifies the observed trend to stiffer and stronger materials, and simultaneously to high glass transition temperatures, with increasing lignin content.

The use of low molecular weight, high lignin-content and unfractionated lignin epoxides has shown to be especially promising. These materials can be handled as liquid prepolymers without the use of solvents, and they yield stiff and strong thermosets having high glass transition temperatures.

ACKNOWLEDGEMENT

This study was financially supported by a grant from the USDA/CSRS (grant #8701415) and by the Center for Adhesive and Sealant Science (CASS) of Virginia Tech.

REFERENCES

1) The previous article of this series appeared in ACS Symp. Ser. 397, 515 (1989), and earlier contributions were published in J. Appl. Polym. Sci., J. Wood Chem. Technol., and Holzforschung, among others.

2) To whom all correspondence should be sent.

3. W.G. Glasser and S.S. Kelley. Lignin. Section in Enc. Polym. Sci. Eng., Wiley & Sons, New York, NY, Vol. 8, 795-852, 1987.

4. T.K. Kirk, T. Higuchi, and H.-M. Chang, eds., Lignin Biodegradation-Microbiology, Chemistry, and Potential Applications. 2 volumes, CRC Press, Inc., Boca Raton, Fl., 1980.

5. H.H. Nimz. In Wood Adhesives, A. Pizzi., ed. Marcel Dekker, New York, NY, page 247-288, 1983.

6. W.G. Glasser. In Adhesives from Renewable Resources, R.W. Hemingway and A.H. Conner, eds., ACS Symp. Ser. 385, 43-54, 1989.

7. J.H. Lora, C.F. Wu, E.K. Pye, and J.J. Balatinecz. Chapter 23 in Lignin-Properties and Materials, W.G. Glasser and S. Sarkanen, eds., ACS Symp. Ser. 397, 312-323, 1989.

8. P.M. Cook and T. Sellers, Jr. Chapter 24 in Lignin-Properties and Materials, W. G. Glasser and S. Sarkanen, eds., ACS Symp. Ser. 397, 324-333, 1989.

9. W.G. Glasser, O.H.-Hsu, D.L. Reed, R.C. Forte, and L.C.-F. Wu. In Urethane Chemistry and Applications, K.N. Edwards, ed., ACS Symp. Ser. 172, 311-338, 1981.

10. S. Hirose, S. Yano, T. Hatakeyama and H. Hatakeyama. Chapter 29 in Lignin-Properties and Materials, W.G. Glasser and S. Sarkanen, eds., ACS Symp. Ser. 397, 382-389, 1989.

11. R. Morck, H. Hatakeyama, H. Yoshida, K. Nakamura. Lignin-Based Polyurethanes. Project 4.1, Final Report to the Swedish National Board for Technical Development, STU-information No. 778, 1990, 78 pg.

12. S.S. Kelley, W. G. Glasser, and T.C. Ward. Chapter 31 in Lignin-Properties and Materials, W.G Glasser and S. Sarkanen, eds., ACS Symp. Ser. 397, 402-413 (1989).

13. W.G. Glasser and H.-X. Wang. Chapter 41 in Lignin-Properties and Materials, W. G. Glasser and S. Sarkanen, eds. ACS Symp. Ser. 397, 515-522 (1989).

14. S. Tai, M. Nagata, J. Nakano, and N. Migita. Mokuzai Gakkaishi, 13, 102 (1967).

15. S. Tai, J. Nakano, and N. Migita. Mokuzai Gakkaishi 13, 257 (1967).

16. G.F. D'Alelio. US-Pat. #3,905,926, 1975.

17. D.B. Holsopple, W.W. Kurple, W.M. Kurple, and K.R. Kurple, US-Pat., #4,265,809, 1981.

18. W.Nieh and W.G. Glasser. In Lignin-Properties and Materials, W.G. Glasser and S. Sarkanen, eds., ACS Symp. Ser. 397, 506-514 (1989).

19. W.G. Glasser, W. de Oliveira, and W.L.-S. Nieh. US-Pat., #4,918,167, 1990.

20. N. Shiraishi, H. Ito, and N. Tsujimoto. J.P. 61, 215, 678 (86, 215, 678) through Chem. Abstr. 106, 85296 m (1987).

21. Cr. I. Simionescu, G. Cazacu and M.M. Macoveanu. Cell. Chem. Technol. 21, 525-534 (1987).

22. F.T. Ball, W.K. Doughty, and H.H. Moorer. Can. Pat. #654, 728 (1962).

23. D. Feldman, D. Banu, C. Luchian, and J. Wang. J. Appl. Polym. Sci. 42, 1307-1318 (1991).

24. B. Tomita, K. Kurozumi, A. Takemura, and S. Hosoya. Chapter 39, In Lignin-Properties and Materials, W. G. Glasser and S. Sarkanen, eds., ACS Symp. Seri. 397, 496-505 (1989).

25. K. Hofmann, "Synthesis, Properties, and Morphology of Lignin-Based Epoxy Resins", Ph.D. Thesis, Virginia Tech, Blacksburg, 1991.

26. W.G. Glasser. In Proc. Intl. Symp. Wood Pulp. Chem., Melbourne, Australia, April 29-May 3, 319-322, 1991.

27. S.S. Kelley, W.G. Glasser, T.C. Ward. J. Wood Chem. Technol., 8, 341-359, 1988.

28. W. de Oliveira and W.G. Glasser. J. Appl. Polym. Sci., 37, 3119-3135, 1989.

29. L.C.-F. Wu and W.G. Glasser. J. Appl. Polym. Sci., 29, 1111-1123, 1984.

30. ASTM D1652-73 (reapproved 1980).

31. E.J. Siochi, T.C. Ward, M.A. Haney, and B. Mahn. Macromolecules, 23, 1420-1429, 1990.

32. Only those arms carrying epoxides will become effective network chains upon cross-linking. However, epoxy-free poly(alkylene oxide) chains will have an effective plasticizing effect on the thermoset.

33. S.I. Falkehag. *Appl. Polym. Symp.*, 28, 247-257, 1975.