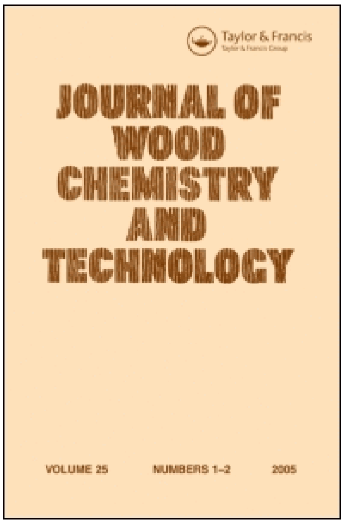

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Engineering Plastics from Lignin. X. Enthalpy Relaxation of Prepolymers

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ENGINEERING PLASTICS FROM LIGNIN.
X. ENTHALPY RELAXATION OF PREPOLYMERS[1]

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Dedicated to Prof. J. L. McCarthy on the Occasion of his 70th Birthday

ABSTRACT

A linear relationship between the enthalpy relaxation and the logarithm of time was observed for a variety of lignins and lignin derivatives annealed at temperatures below their glass transition temperature. While the behavior is noticeably affected by differences in lignin structure in terms of origin, chemical functionality and molecular weight, the sub-Tg annealing temperatures were found to be the primary factor determining the rate d ER/d log t (where ER represents enthalpy relaxation and t time), and this ranged from 0.2 to 0.4. This time dependent reduction in enthalpy is the result of a non-equilibrium chain conformation and has been shown to correlate with mechanical and several other physical properties for a number of material systems.

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INTRODUCTION

The physical aging of an amorphous polymer is essentially a gradual continuation of the vitrification that occurs when a polymer is cooled through its glass transition temperature, T_g. When a polymer is cooled from the melt, the rapid rise in viscosity that occurs as T_g is approached freezes the polymer chains in a non-equilibrium conformation and configuration leaving an excess free volume quenched into the system. The physical aging phenomenon is seen to result from the relaxation of the polymer chains, eliminating the excess free volume, in an effort to approach the preferred, or true equilibrium state of the system[3]. Consequently, this behavior is manifested through a slow decrease in volume (densification), enthalpy (enthalpy relaxation), or other state function variables. Because of the convenience and accuracy in detecting changes in heat capacity by differential scanning calorimetry (DSC), the enthalpy relaxation is often utilized to monitor the physical aging phenomenon in amorphous glasses[4-6].

Considering that physical aging is simply continuing vitrification, it is not surprising that it affects, in the same direction, those material properties that are drastically altered upon cooling a polymer through its T_g. Loss of ductility, increased brittleness, reduced damping, and reduced rate of stress relaxation are often associated with physical aging of polymeric materials[7-9]. Enthalpy relaxation has been demonstrated to correlate with a number of time-dependent mechanical and dielectric properties. Most research on this phenomenon has dealt with linear polymers such as polycarbonate[11-13] and poly(ethylene terephthalate)[6,8,14] with more recent work on epoxy[15] and polyurethane[14] networks. However, the redistribution of free volume in glasses is common to all amorphous materials and is receiving increased attention due to its influence on material properties, as well as implications of organization in amorphous polymers.

As an amorphous polymer, lignin is extremely sensitive to thermal history since it also exhibits enthalpy relaxation. This fact has been recognized only recently and is responsible for much of the disagreement of lignin Tg reports in the literature[17,18]. The changes in heat capacity of lignins annealed at around their Tg were first observed by Hatakeyama, et al.[19] in the form of endothermic peaks in the DSC curves of lignin at their glass transition. This peak was found to increase with both annealing time and temperature, and differences in the rates of enthalpy relaxation were attributed to hydrogen bonding involving phenolic hydroxy groups.

It was the goal of this study to evaluate both the effect of various structural parameters of the lignin prepolymer and of the thermal history of the sample on the enthalpy relaxation behavior. Differences in the nature of the lignins were in regard to origin, chemical functionality, and molecular architecture. Although only few material properties can be measured directly on these lignin prepolymers owing to their low molecular weight nature, it must be suspected that several of their characteristic features influence the properties of materials made from them[20].

MATERIALS

1. Milled Wood Lignin (MWL):

MWL from red alder sapwood was obtained from Wiley-milled and extracted wood meal that was milled with steel balls for two weeks[21]. The lignin was isolated by solvent extraction with 90% aqueous dioxane, and it was purified by the procedure of Bjorkman[22].

2. Kraft Lignin (KL):

KL was prepared from a commercial Indulin ATR sample by Westvaco (North Charleston, South Carolina) by dissolving it in alkali and acid precipitation (5 N HCL), filtration, washing, and freeze drying.

3. Steam Explosion Lignin (SEL):

An SEL preparation from aspen was obtained from a pilot plant operated by Iotech Corporation of Ottawa, Ontario, Canada. This sample was obtained by alkali extraction, acid precipitation, and drying.

4. Organosolv Lignin (OSL):

Two OSL preparations, one from aspen and one from pine, were obtained from Biological Energy Corporation of Valley Forge, PA, and the samples were used as received.

5. Hydroxypropyl Lignin Derivatives (HPL) [23]:

An HPL derivative from OSL-aspen was prepared in toluene at 170°C using 1.3 ml propylene oxide per gram of lignin and 3% KOH on lignin as catalyst, in a 300 ml Parr reactor. An HPL derivative from OSL-pine was prepared in aqueous alkali at room temperature for two days, using a four-fold excess of propylene oxide to lignin weight. The derivative was precipitated by acidification, and isolated by filtration.

METHODS

1. Differential Scanning Calorimetry (DSC):

A Perkin-Elmer Model DSC-4 interfaced with a Thermal Analysis Data Station was used for determination of thermal properties of the samples. The glass transition temperature was defined as one-half the change in heat capacity that occurs over the transition. In order to eliminate the effect of moisture and thermal history, samples were first scanned above T_g and held there for 5 minutes before cooling to room temperature. Samples were then annealed below T_g under a nitrogen purge for various time periods. Heating and cooling rates remained constant at 10°C min^{-1}.

2. Measurement of Enthalpy Relaxation:

The extent of enthalpy relaxation in a sample was determined by superimposing the DSC curves of the annealed sample with the endothermic peak on that of the quenched sample exhibiting a normal secondary transition (Figure 1). Because of slight differences in heat capacity in the glassy region, greatest attention was given to matching the curves in the region above T_g. The area under the peak then gives the reduction in enthalpy that has occurred. Instrument calibration was accomplished using indium.

RESULTS AND DISCUSSION

1. Lignin Structures:

Seven different lignin and lignin derivative preparations were selected for this study. These samples represent a spectrum of significant differences in regard to chemical functionality, type and frequency of bonding between individual, lignin-building (C_9)

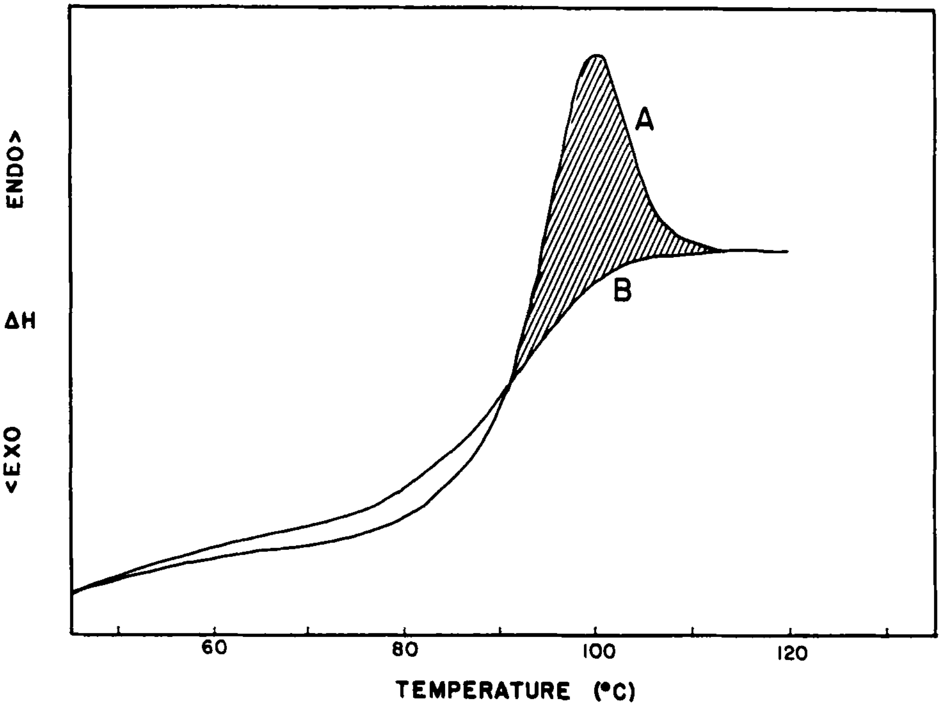

Figure 1. Typical DSC Traces of a Hydroxypropyl Lignin Derivative: a) Annealed and b) Quenched.

units, in relation to the degree of substitution of the unifunctional hydroxypropyl derivatives, in relation to molecular weight and weight distribution, and in relation to thermal properties. These seven different lignins selected covered a range of glass transition temperatures (T_g) between 58 and 172°C, and molecular weights (M_w) between about 1000 and 8000 gM^{-1}. Several of the structural and macromolecular characteristics of the samples are summarized in Table 1.

2. The Enthalpy Relaxation Phenomenon:

The phenomenon of enthalpy relaxation is one common to all amorphous glassy materials whether of low

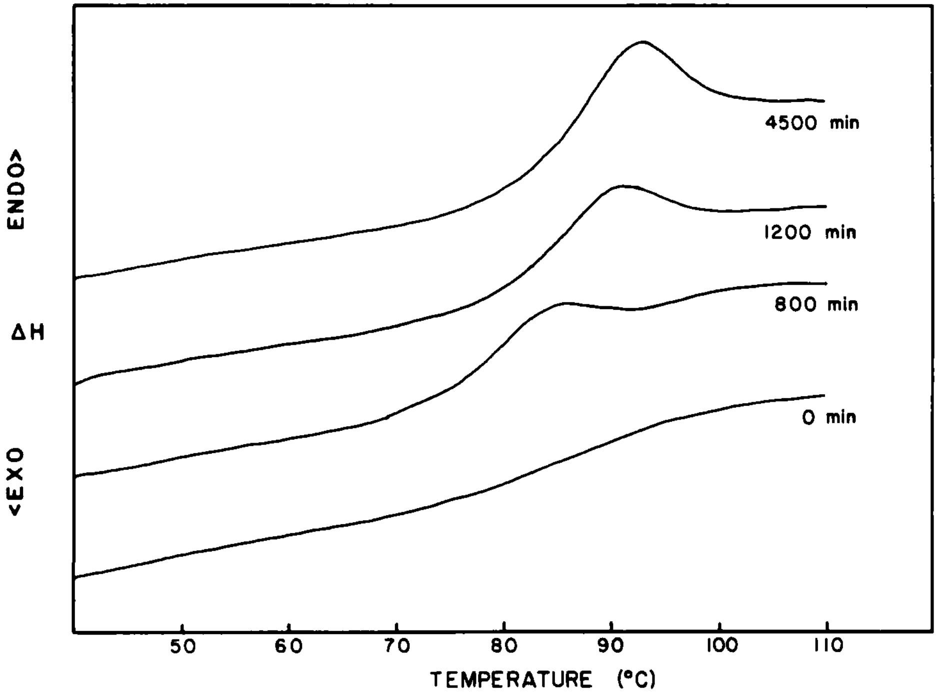

Figure 2. The Effect of Annealing Time on the DSC Traces of a Hydroxypropyl Lignin Derivative.

or high molecular weight. Generally, as a material is cooled through its glass transition temperature, the rapid rise in viscosity quenches an excess of free volume into the system. As a consequence of the attractive energy between neighboring molecules, this necessarily leads to an excess internal energy. Owing to localized molecular motion in the glassy state, this excess free volume is eliminated, thereby reducing the internal energy and enthalpy of the molecular system[3].

Figure 2 illustrates the enthalpy relaxation phenomenon in lignin as determined by DSC. From this, several qualitative observations can be reiterated.

TABLE 1

Structural and Molecular Characteristics of Lignin and Lignin Derivative Preparations

	Structural Characteristic	MWL[1] (Red Alder)	KL[1] (Pine)	SEL[1] (Aspen)	OSL[1] (Aspen)	OSL[1] (Pine)	HPL[2] (OSL-Aspen)	HPL[2] (OSL-Pine)
I.	FUNCTIONALITY							
	(per C_9)							
	Total OH	1.09	1.32	1.14	1.09	1.15	2.2	1.6
	Phenolic OH	0.39	0.59	0.49	0.59	0.64	0.0	0.0
	SYR:GUA Ratio	1.2	na	1.8	1.0	na	na	na
	OCH	1.36	0.81	1.13	1.03	0.77	na	na
II.	LINKAGES (per C_9)							
	Hydrolysis Factor	0.22	0.83	0.52	0.87	0.87	na	na
	Al-0-4	0.55-0.65	0.05-0.10	0.28-0.32	0.03-0.08	0.03-0.08	na	na
	1/5-5, 4-0-5	0.17-0.22	0.40-0.45	0.17-0.22	0.20-0.25	0.32-0.37	na	na
	A1-2/6	0.02-0.04	0.07-0.10	0.06-0.08	0.15-0.20	0.10-0.15	na	na
	A1-5	0.02-0.05	0.10-0.15	0.02-0.05	0.02-0.06	0.07-0.12	na	na
III.	MOLECULAR PARAMETERS							
	M_n (VPO)	2,700	1,500	1,200	1,200	800	--	--
	M_n (SEC)	1,200	1,300	800	600	500	900	600
	M_w (SEC)	7,700	4,300	2,300	2,100	1,400	4,900	2,500
	T_g (DSC)[3]	172	159	163	98	90	58	87

[1] According to Glasser et al. (24,25).

[2] According to Glasser et al. (26).

[3] Differences in T_g between this study and earlier reports (24, 26) must be attributed to the use of different sample preparations.

First, as the sub-T_g annealing time is increased, the endothermic peak (associated with the enthalpy relaxation) grows in intensity and is shifted to higher temperatures. In addition, the onset of T_g is shifted to slightly higher temperatures since molecular motion is restricted by the reduction of free volume. Finally, although the curves are offset along the ordinate for illustration, it was noted that the heat capacity of the material in the glassy region was lowered as annealling time increased. This indicates a reduction in the vibrational freedom of the lignin which suggests that organization of the polymer chains may play a role in the relaxation, as well as changes in free volume.

3. <u>Effects on Enthalpy Relaxation</u>:

The rate at which heat capacities of lignins change are clearly related to the temperature level at which annealing is performed. Figure 3 illustrates that the rate of enthalpy relaxation (determined from the slope of the enthalpy relaxation curve vs. log time) reaches a maximum at about 15°C below T_g before dropping off rapidly as the annealing temperature approaches the glass transition. This point essentially identifies the onset of T_g with a higher equilibrium free volume reducing the extent of relaxation in the system.

The influence of lignin type on enthalpy relaxation and its rate are illustrated in Figure 4. In an effort to eliminate temperature effects, all samples were annealed at 27°C below their T_g. OSL-aspen is found to relax faster than any other lignin preparation, and approximately 40% faster than kraft lignin. OSL-pine and SEL relax at a rate about equal

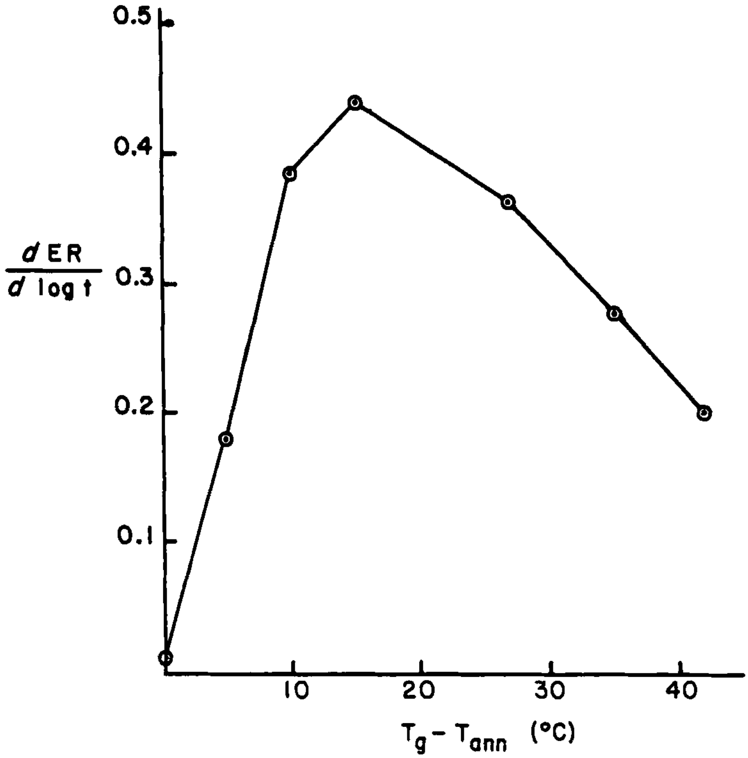

Figure 3. The Variation in the Rate of Enthalpy Relaxation with Sub-T_g Annealing Temperature.

or slightly faster than that of kraft lignin. Although significant differences in the relaxation rate seem to exist between different lignins, they are not clearly related to any structural or macromolecular characteristic. Even unifunctional (aliphatic OH groups, only) hydroxypropyl lignin derivatives with widely different degrees of substitution exhibit enthalpy relaxation behavior indistinguishable from that of lignins (Figure 5). Although the OSL-pine derivative relaxes about 40% faster than KL, the OSL-

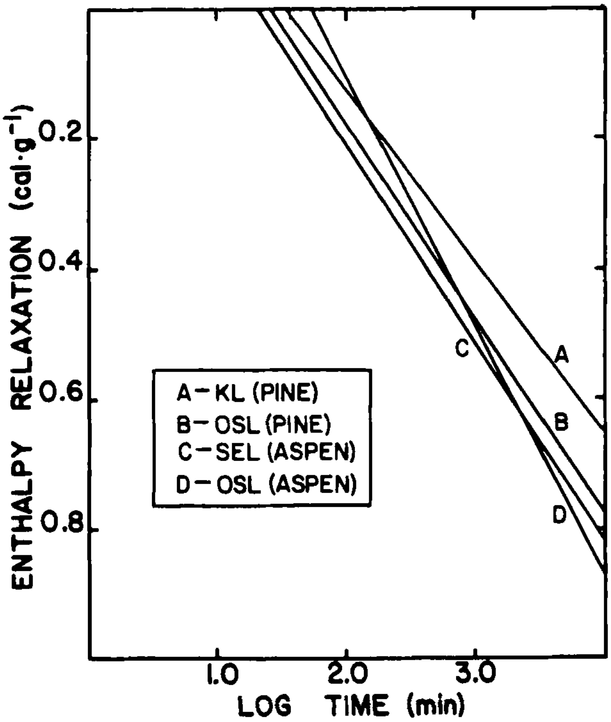

Figure 4. Comparison of Enthalpy Relaxation for Various Lignins Annealed at 27°C Below Their Glass Transition.

aspen derivative is about 10% slower. This experiment illustrates that there is no consequence on the enthalpy relaxation phenomenon by lignin's phenolic hydroxy functionality. Hydrogen bonding via phenolic OH groups has earlier been held responsible for changes in heat capacity in relation to sub-T_g annealing.

Table 2 summarizes the enthalpy relaxation rate data in comparison to that for cured epoxy resin. Even the epoxy sample fails to be drastically different (only 14% slower relaxing than KL) than the lignin preparations. This observation is consistent with the

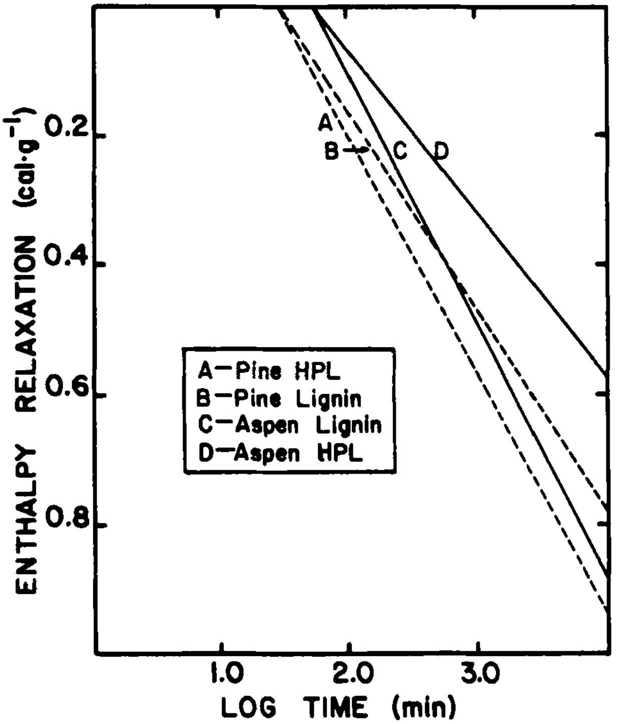

Figure 5. Comparison of an Organosolv Pine and Aspen Lignin and Their Hydroxypropyl Derivatives.

TABLE 2

Summary of Enthalpy Relaxation Data for Various Lignins and Lignin Derivatives Annealed at 27°C Below Their Glass Transition Temperature

SAMPLE	T_{ann} (°C)	No. of Points	R^2	Regression Model		Δ Slope[3]
				Intercept	Slope	
MWL (Red Alder)	145	4	1)	1)	1)	1)
KL (Pine)	132	7	0.87	-0.4145	0.2670	100
SEL (Aspen)	136	5	0.99	-0.3967	0.3037	114
OSL (Aspen)	71	7	0.94	-0.6538	0.3830	143
OSL (Pine)	63	6	0.93	-0.4338	0.3015	113
HPL (OSL-Aspen)	31	5	0.94	-0.4186	0.2469	92
HPL (OSL-Pine)	60	5	0.92	-0.5750	0.3708	137
Epoxy[2]	60	4	0.96	-0.2328	0.2294	86

[1] MWL (Red Alder) exhibited a continual increase in T_g with annealing introducing error into the temperature difference between T_g-T_{ann}.

[2] Data from Ophir, et al. (15), on unmodified Epon 828 Epoxy.

[3] Change of slope with respect to KL (in %).

premise that while chemical structure may influence enthalpy relaxation, within a particular aging range the phenomenon proceeds in a very similar manner in all glassy materials.

CONCLUSIONS

1. Lignins and lignin derivatives, which are beginning to find consideration as prepolymers for solid engineering plastics, were found to undergo enthalpy relaxation at sub-T_g temperatures.

2. The relaxation rate was found to depend on the temperature at which sub-T_g annealing is performed.

3. Although differences between different lignins and lignin derivatives are detectable, they cannot be attributed to a specific structural or macromolecular feature. While OSL-aspen relaxed about 40% faster than KL, OSL-pine, SEL and MWL relaxed at about the same rate or only slightly faster than KL.

4. Unifunctional, non-phenolic hydroxypropyl lignin derivatives relaxed either faster (OSL-pine-HPL) or slower (OSL-aspen-HPL) than KL.

5. All lignins and lignin derivatives relaxed faster than cured epoxy resin, but not more than by a factor of approximately 1.5 to 2.

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REFERENCES

1. Earlier papers in this series have been published in J. Appl. Polym. Sci. and in Holzforschung.

2. The authors are Graduate Research Assistant and Professor of Wood Chemistry, respectively. All correspondence regarding this article should be directed to the second author.

3. L.C.E. Struik, Physical Aging in Amorphous Polymers and Other Materials, p. 1-2, Elsevier, New York, 1978.

4. H. E. Bair, Polym. Eng. Sci., 14, 202 (1974).

5. H. E. Bair, G. H. Bebbington and P. G. Kelleher, J. Polym. Sci.: Polym. Phys. Ed., 14, 2113 (1976).

6. A. Aref-Azar, F. Biddlestone, J. N. Hay and R. N. Haward, Polymer, 24, 1245 (1983).

7. S. S. Sternstein and T. C. Ho, J. Appl. Phys., 43, 4370 (1972).

8. R. M. Mininni, R. S. Moore, J. R. Flick and S. E. B. Petrie, J. Macromol. Sci.-Phys., 138(1-2), 343 (1973).

9. G. Levita and L. C. E. Struik, Polymer, 24, 1071 (1983).

10. S. Matsuoka, C. J. Aloisio and H. E. Bair, J. Appl. Phys., 44, 4265 (1973).

11. D. G. Legrand, J. Appl. Polym. Sci., 13, 2129 (1969).

12. K. Neki and P. H. Geil, J. Macromol. Sci-Phys., 138(1-2), 295 (1973).

13. M. H. Litt and S. Torp, J. Appl. Phys., 44, 4282 (1973).

14. E. Ito, K. Tajima and Y. Kobayashi, Polymer, 24, 877 (1983).

15. Z. H. Ophir, J. A. Emerson and G. L. Wilkes, J. Appl. Phys., 49, 5032 (1978).

16. U. Yilmazer and R. J. Farris, J. Appl. Polym. Sci., 28, 3269 (1983).

17. H. Hatakeyama, K. Kubota and J. Nakano, Cell. Chem. Tech., 6, 521 (1972).

18. D. A. I. Goring, in Lignins, Chap. 17, K. V. Sarkanen and C. H. Ludwig (eds.), Wiley Interscience, New York, 1971.

19. T. Hatakeyama, K. Nakamura and H. Hatakeyama, Polymer, 23, 1801 (1982).

20. T. G. Rials and W. G. Glasser, Holzforschung, in press.

21. W. G. Glasser and C. A. Barnett, Holzforschung, 33, 78 (1979).

22. A. Bjorkman, Sven. Papperstidn., 59, 477 (1956).

23. W. G. Glasser, L. C.-F. Wu, and J.-F. Selin, In "Wood and Agricultural Residues", E. J. Soltes (Ed.), p. 149-166, Academic Press, New York (1983).

24. W. G. Glasser, C. A. Barnett, P. C. Muller and K. V. Sarkanen, J. Agric. Food Chem., 31, 921 (1983).

25. W. G. Glasser, C. A. Barnett and Y. Sano, Appl. Polym. Symp., 37, 441 (1983).

26. W. G. Glasser, C. A. Barnett, T. G. Rials, and V. P. Saraf, J. Appl. Polym. Sci., in press.