Polymer Bulletin 12, 1-5 (1984)

Polymer Bulletin

Engineering

Engineering Plastics from Lignin
11. Hydroxypropyl Lignins as Components of Fire Resistant Foams

Wolfgang G. Glasser and Robert H. Leitheiser

Department of Forest Products, and Polymer Materials and Interfaces Laboratory,
Virginia Polytechnic Institute and State University, Blacksburg, VA 24061;
and The Quaker Oats Company, Barrington, IL 60010, USA

SUMMARY

Low density polyurethane foams (ca. 2 lbs./cu. ft.) with acceptable strength and excellent flammability resistance properties were formulated with a commercial furan polyol containing 20% hydroxypropyl lignin derivative. Propylene oxide-modified lignin from two sources, kraft and organosolv lignin, were employed. The organosolv lignin derivative exhibited better foaming characteristics than the corresponding kraft lignin, which collapsed when the rising foam was touched for testing. The weight contribution of lignin derivative was limited to 20% by compatibility with the fluorocarbon blowing agent, and solubility in polyol. Preliminary tests encourage further research on structural materials containing hydroxypropyl lignin derivatives.

Introduction

The manufacture of structural materials on lignin basis provides an opportunity for utilizing renewable resources for materials which are normally produced from fossil carbon sources (1). Various lignin derivatives have previously been shown to function well in polyurethanes (2-7). Foams (2,3), coatings (4,5), adhesives (4,6), and films (7) with a wide range of performance characteristics have been synthesized using propylene oxide-modified lignins from various sources.

This study reports the results of preliminary tests in which the use of hydroxypropyl lignin was examined as component and extender of a commercial furan polyol product formulated into a Class I fire resistant foam with an aromatic polyisocyanate.

Experimental

Furan Polyol: A commercial furan polyol, FaRez® 6305 by The Quaker Oats Company, Barrington, IL, was the basic polyol component.

Hydroxypropyl Kraft Lignin: This was prepared from a commercial kraft lignin preparation, Indulin® AT by Westvaco Corp., by hydroxypropylation in aqueous NaOH at room temperature according to Glasser et al. (8). The product had a hydroxyl content of 6.6% and a moisture content of 4.6%.

Hydroxypropyl Organosolv Lignin: This was prepared from an organosolv (aqueous ethanol/H_2SO_4) lignin preparation from aspen obtained from Biological Energy Corp. of Valley Forge, Pa. It was derivatized at room temperature in aqueous NaOH according to an earlier procedure (8). Its hydroxyl content was 5.4%, and it contained 3.7% moisture.

Test Methods: Foam samples were prepared by blending ingredients in a 32 oz. paper cup using a 5400 rpm electric stirrer. The blended foam mix was immediately poured into a 6" x 12" x 4" cardboard box lined with aluminum foil. Cream, gel and rise times were measured and recorded.

Foam samples were cut out after 48 hours from the foam bun. Physical properties measured were density, friability using the ASTM C-241 tumbling test, and compressive strength as per ASTM D-1621. Flammability tests were run using the Mobile 45° Angle Flammability test. This test procedure utilizes a 2" x 8 1/2" x 1/2" specimen mounted edgewise at a 45° angle.

Flame is applied to the lower corner until visible flaming ceases. Sample weight loss has been found to correlate well with E-84 tunnel flame spread ratings. For FaRez® 6305 foam without added flame retardants, a percent weight loss of 70.4 corresponds to an E-84 flame spread rating of 35. With bromide and phosphorus flame retardants, FaRez® 6305 gives E-84 FS ratings of <25. These blends of FaRez® 6305 and propoxylated lignins should behave similarly.

Results and Discussion

Polyurethane foam samples for use in tests regarding their resistance to flammability, and useful in structural applications, were prepared from hydroxypropyl lignin-extended furan polyol with an aromatic polyisocyanate using a routine foam synthesis. Formulation parameters are listed in Table 1. The lignin derivative content was kept constant at 20% by weight after it was discovered in preliminary trials that larger amounts of lignin resulted in an inhomogeneous mixture

TABLE 1. FOAM FORMULATION DATA
(in parts by weight)

	CONTROL	KRAFT HPL	ORGANOSOLV HPL
POLYOL:			
Furan-HPL1)	100	80	80
Lignin-HPL2)	-	20	20
ISOCYANATE:			
Polymeric Isocyanate3)	133.7	138.1	130.9
ADDITIVES:			
Silicone Surfactant4)	2.0	2.0	2.0
Amine Catalyst5)	1.3	1.6	2.4
Blowing Agent6)	32.0	30.7	32.0

1) Furan polyol FaRez® 6305 by The Quaker Oats Company
2) Prepared by room temperature (aqueous alkali) propoxylation according to ref. 8.
3) Upjohn Papi® 135
4) Dow Corning Q2-5103
5) Abbott Laboratories Polycat® 8
6) E. I. duPont Freon® F-11

of base polyol, fluorocarbon blowing agent, and lignin derivative. This non-uniformity was found to prevent the preparation of suitable foams. The solubility of alkoxylated lignin derivatives varies significantly with the chemical and molecular nature of the preparation, and this has been pointed out previously (9). Type of alkylene oxide, degree of substitution, reaction conditions, nature and source of lignin, etc. all result in differences in prepolymer character and solubility property.

Data regarding polyol reactivity and foam properties are listed in Table 2. The results indicate that good, stable foams can be prepared with the lignin extended furan polyol, especially with the organosolv lignin derivative. Kraft HPL rose satisfactorily during foam synthesis but collapsed when the rising, uncured foam ("bun") was touched for the purpose of checking gel time. This difference in response between the organosolv and kraft lignin containing foam may possibly be explained with differences in molecular or chemical structure (functionality) between the two lignin preparations. Kraft lignin is somewhat higher in molecular weight and molecular weight distribution, and it contains a significant amount of thiol groups. Differences between these two lignins have recently been summarized (10). Because the kraft lignin-containing foam collapsed during preparation, and the foam shrank visibly in the area of contact, the resultant product had a higher overall density and consequently a higher

TABLE 2. FOAM REACTIVITY AND PROPERTIES DATA

	CONTROL	KRAFT HPL	ORGANOSOLV HPL
<u>Reactivity</u>:			
Cream time, sec	30	27	23
Firm time, sec	57	87	70
Tack free time, sec	87	100	90
Rise time, sec	99	100	90
Exotherm, °C	146	114	117
<u>Properties</u>:			
Density, lb/cu. ft.	2.2	3.43[1)]	2.26
Compressive strength,			
Parallel, psi	29.2	38.2	16.6
Perpendicular, psi	18.2	38.4	19.5
Tumbling Friability (10 min), % wt loss	4.3	13.4	2.4
Flammability Resistance[2)]			
Mobil 45°, % wt loss	70.4	65.5	69.4

[1)] Foam collapsed when the bun was touched to check gel time.

[2)] The flammability test results are laboratory evaluations for comparing one foam system to another. The results cannot be used to predict performance under actual fire conditions.

compressive strength as compared to both the control and the organosolv lignin foam product.

The data in Table 2 indicate that both lignin containing foams gave lower parallel compressive strength than the lignin-free control sample, but that perpendicular compressive strength and friability were equal to or superior than the unextended control. The simple Mobil 45° flammability test has been found previously, in the industrial test laboratory of The Quaker Oats Company, to be more useful than the more frequently used ASTM D-1692-59T standard which employs the same size specimen, but in which the sample is mounted horizontally on a wire screen. Where correlation between the Mobile 45° test and the UL's Northbrook E 84 tunnel test is generally excellent, correlation with the ASTM D-1692-59T test has been poor. When the lignin containing foams were subjected to the Mobil 45° flammability test, results indicated a small but clearly noticeable increase in fire resistance over the lignin-free control polyurethane foam. The significance of this increase however requires further research. These data however suggest that hydroxypropyl lignin derivatives, especially if their solubility properties can be further improved, have the potential of serving usefully as extenders for fire resistant polyurethane foam products.

Conclusions

Propoxylated lignin derivatives are found to constitute useful extenders for fire resistant polyurethane foams for structural applications. Preliminary results suggest that their weight contribution is limited to about 20% of total polyol, and that this limitation is based on the derivatives' compatibility with the fluorocarbon blowing agent and the furan polyol. The lignin containing foams appeared to have good stability, especially if a sulfur-free (organosolv) lignin derivative was employed. Foam compressive strength was weakened parallel to the direction of rise by the presence of lignin component; and it was equal to the control in the perpendicular direction. Flammability resistance of the lignin-containing foam displayed a slight increase over the control sample, but the significance of this result requires further study.

Acknowledgement

This study was financially supported by a grant from the National Science Foundation, Renewable Materials Engineering Program. Valuable assistance with sample preparation was provided by Ms. Charlotte A. Barnett of VPI & SU, and this is acknowledged with gratitude.

References

1. S. I. Falkehag, Appl. Polym. Symp. 28, 247-257 (1975).
2. H. H. Moorer, W. K. Dougherty, and F. J. Ball, U.S. Patent 3,519,581 (1970).
3. O. H.-H. Hsu and W. G. Glasser, Appl. Polym. Symp. 28, 297-307 (1975).
4. O. H.-H. Hsu and W. G. Glasser, Wood Sci. 9(2), 97-103 (1976).

5. L. N. Mozheiko, M. F. Gromova, L. A. Bakalo, and V. N. Sergeyeva, Polymer Sci. USSR 23(1), 149-155 (1981).
6. W. G. Glasser, V. P. Saraf, and W. H. Newman, J. Adhesion 14, 233-255 (1982).
7. V. P. Saraf and W. G. Glasser, J. Appl. Polym. Sci. 29(5), 1831-1841 (1984).
8. W. G. Glasser, L. C.-F. Wu, and J.-F. Selin, in "Wood and Agricultural Residues: Research on Use for Feed, Fuels, and Chemicals", E. J. Soltes, ed., Academic Press, New York, 149-166 (1983).
9. W. G. Glasser, C. A. Barnett, T. G. Rials, and V. P. Saraf, J. Appl. Polym. Sci. 29, 1815-1830 (1984).
10. W. G. Glasser, C. A. Barnett, P. C. Muller, and K. V. Sarkanen. J. Agric. Food Chem. 31(5), 921-930 (1983).

Accepted July 3, 1984