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POLYFUNCTIONAL ION-EXCHANGERS BASED ON WOOD

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α-Oxide wood derivatives were synthesized by O*-alkylation of wood with a bifunctional epoxide oligomer in the presence of* Et_3N *catalyst. Polyfunctional ion-exchangers were prepared by subsequent amination of them by aliphatic polyamines.*

Key words: wood, epoxide oligomer, polyamines, chemical modification, alkylation, ion-exchanger, static exchange capacity.

The goal of the present work was to synthesize and investigate anion-exchangers based on wood by esterifying it with the diglycidyl ether of dihydroxydiphenylpropane (DGEDHDPP) and subsequent amination with aliphatic polyamines.

The α-oxide wood derivatives were synthesized by reacting hydroxyls of the natural polymer with the oxirane rings of the diglycidyl oligomer. This formed ethers (**1**) and grafted (**2**) and linked (**3**) copolymers containing free epoxides.

Previous investigations found that the uncatalyzed reaction of the α-oxides with natural hydroxy-containing polymers is typically slow and inefficient [1]. Wood etherification by the diepoxide was performed in the presence of Et_2N (TEA) catalyst (Table 1).

The content of α-oxidic group chemically bound to the wood surface increased with increasing mole fraction of tertiary amine in the epoxidizing mixture. Their content reached a maximum at a ratio close to equimolar. Further increasing the TEA concentration does not increase the epoxide number, weight gain, and C content in the modified products. This was due to extensive side reactions of DGEDHDPP in the presence of a large excess of amine. This was primarily di- and trimerization of the diglycidyl oligomer.

The distributions of epoxides in the main and side reactions indicated that increasing the catalyst content above equimolar did not substantially increase the fraction of oxirane rings consumed in direct reaction with the wood (Table 1). The relative amount of α-oxidic group involved in side reactions increased continuously and exceeded the number of unreacted glycidyl rings. A consequence of these reactions was the relatively constant elemental composition of the etherified lignocellulose formed in an excess of organic base.

The significant weight gain observed with these catalyst concentrations suggested that anionic grafting polymerization of the polyglycidyl compounds occurred on the wood surface (**2** and **3**). This was indirectly indicated by the equilibrium swelling of the alkylated wood, which sharply increased compared with that of the initial wood by seven times (Table 1).

IR spectra of the modified samples confirmed that glycidyl derivatives were formed. In contrast with spectra of the starting activated polymer, they contained new absorption bands at 1250 and 831 cm^{-1}, which were consistent with an oxirane ring in the etherified lingocellulose. According to the literature [2, 3], these are due to C–C deformations in a three-membered ring.

Epoxidized samples with the maximum content of α-oxidic group were aminated with high-molecular-weight amines, polyethyleneimine (PEI) and polyethylenepolyamine (PEPA), in order to prepare wood with anion-exchanger properties. Table 2 shows that the static exchange capacity (SEC) of the lignocellulose ion-exchangers increased regularly with increasing content of aminating agent in the starting reaction mixture. The highest SEC values were observed for mass ratios of modified wood to PEI and PEPA of 1.0:1.0 and 1.0:0.5, reaching 5.73 and 4.27 mg·equiv/g with an active N content of 8.02 and 5.98%, respectively. Further increasing the amount of polyamine did not increase the SEC but caused the formation of polyelectrolytes in low yield and with high moisture content and unsatisfactory mechanical strength.

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TABLE 1. Synthesis of α-Oxide Wood Derivatives ($T = 100°C, \tau = 1$ h, γ = equilibrium swelling)

Epoxide:TEA, mol	Epoxide content, %	Wt. gain, %	Elemental composition, %				γ, %	Amount of epoxides consumed in reaction, %		
			C	H	N	O		main	side	unconverted
1.0:0.00	0.12	0.80	46.85	5.88	0.87	46.40	54.4	2.42	0.30	97.28
1.0:0.05	1.83	2.63	50.12	6.36	1.93	41.59	69.5	7.87	1.20	90.93
1.0:0.1	2.40	10.27	50.35	6.56	2.04	41.05	72.5	31.08	4.50	64.42
1.0:0.3	3.90	18.00	50.74	6.47	2.29	40.50	110.0	54.46	6.00	39.54
1.0:0.5	4.61	21.17	53.67	7.46	2.53	36.34	300.0	66.70	7.20	26.10
1.0:1.0	4.33	24.00	55.38	7.53	2.50	34.59	386.6	72.61	8.40	18.99
1.0:1.5	4.06	24.10	55.44	7.26	2.46	34.84	394.0	72.91	9.60	17.49
1.0:2.0	3.83	24.18	55.67	7.46	2.36	34.51	396.4	73.16	10.70	16.14
1.0:3.0	3.44	24.25	55.83	7.28	2.08	34.81	390.9	73.38	11.60	15.02
1.0:4.0	3.06	24.37	55.37	7.00	2.04	35.59	385.5	73.74	12.60	13.66
1.0:5.0	2.80	24.42	55.70	7.02	2.02	35.26	381.0	73.88	13.34	12.78

TABLE 2. Effect of Reactant Ratio on Composition and Physical Chemical Properties of Lignocellulose Ion-Exchangers ($T_{amination} = 80°C$, $\tau_{amination} = 3$ h, $T_{solidification} = 80°C$, $\tau_{solidification} = 10$ h)

Epoxidized wood:polyamine, mass part	SEC in HCl (0.1 N), mg·equiv/g	N content, %		Moisture, %	Yield, %
		$N_{tit.}$	$N_{tot.}$		
PEI					
1.0:0.25	1.60	2.24	3.65	60.56	99.12
1.0:0.50	2.50	3.50	5.33	68.55	97.35
1.0:0.75	3.70	5.18	7.89	69.59	95.02
1.0:1.0	5.73	8.02	11.03	70.61	93.59
1.0:1.5	5.80	8.12	11.27	72.30	75.68
PEPA					
1.0:0.25	2.85	3.99	5.38	75.43	99.04
1.0:0.50	4.27	5.98	7.56	80.21	98.75
1.0:0.75	4.28	5.99	7.71	80.31	84.64
1.0:1.0	4.30	6.02	7.84	83.04	74.07
1.0:1.5	4.30	6.02	7.80	81.44	59.25

Increasing the amination temperature to 100°C (Table 3) slightly decreased the capacity, yield, moisture content, and active and total N content in the modified polymers. Apparently this was due to the occurrence of parallel side reactions of the epoxides not with amines but with hydroxyls in the system.

According to the literature [4], this reaction is most probable with an increase in the concentration of reagents, temperature, and duration of the process. The alcohol hydroxyls that were formed by the main reaction in a model system consisting of polyglycidylmethacrylate (PGMA) and carboxylic acid in an equimolar ratio at >70°C for 3 h were involved in a side reaction of opening of the PGMA oxirane rings. This included restructuring of the macromolecules of the homopolymer into an insoluble three-dimensionally linked sample. A linear polyether could be prepared at reduced temperature and shorter reaction times.

TABLE 3. Ion-Exchange Capacity of N-Containing Wood Derivatives as a Function of Temperature and Duration of Amination (Epoxidized wood:PEI, 1.0:1.0 by mass; epoxidized wood:PEPA, 1.0:0.50 by mass, $T_{solidification}$ = 80°C, $\tau_{solidification}$ = 10 h)

Modification conditions		SEC in HCl (0.1 N, mg·equiv/g)	N content, %		Moisture, %	Yield, %
T, °C	τ, h		$N_{titr.}$	$N_{tot.}$		
			PEI			
40	3	4.91	6.87	9.53	69.93	75.37
60	3	5.25	7.35	10.37	70.20	86.51
80	3	5.73	8.02	11.03	70.61	93.59
100	3	5.42	7.59	10.87	58.83	90.75
80	1	4.09	5.73	8.12	69.25	87.42
80	2	4.74	6.64	9.13	69.42	91.54
80	4	5.86	8.20	11.48	72.86	96.82
			PEPA			
40	3	4.00	5.60	6.97	73.35	92.96
60	3	4.20	5.88	7.39	78.39	97.83
80	3	4.27	5.98	7.56	80.21	98.75
100	3	4.15	5.81	7.02	56.98	90.00
60	1	3.00	4.20	5.04	76.21	90.15
60	2	3.48	4.87	5.97	78.72	95.62
60	4	4.30	6.02	7.61	84.03	98.22

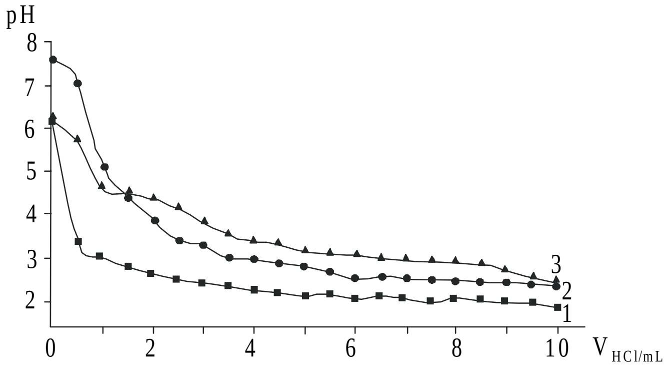

Fig. 1. pH Titration of wood: starting (1) and aminated with PEI (2) and PEPA (3).

Table 3 shows that amination of the α-oxide derivative was practically complete after 3 h at 80 and 60°C for anion-exchangers based on PEI and PEPA, respectively. Increasing the duration of the polymerization reactions increased proportionally the content of total and tritable N, which were responsible for the ion-exchange capacity, indicating that destruction did not occur during the reaction and that the distribution of epoxy—amine crosslinks on the surface of the activated wood was relatively homogeneous. Otherwise, the content of total N would have increased and the activity would have decreased.

The difference in temperatures at which the ion-exchangers with the best physical chemical properties were formed was due to the polymeric nature of the amines used. The higher molecular weight (MW) of PEI compared with PEPA and, consequently, the lower segmented mobility of its macromolecules created significant diffusion barriers to the reaction with wood oxirane rings. Therefore, additional thermal activation was required to drive the reaction in the kinetic region and reach higher degrees of conversion, as reflected in the yield of the desired product.

Potentiometric studies were carried out to evaluate the main properties of the wood anion-exchanger. Figure 1 shows the pH-titration curves of the cellular polyelectrolytes. In contrast with the modified derivatives, the starting wood did not contain functional groups capable of ion exchange. Therefore, they did not act as ion exchangers. The lack of clear inflections and the gentle slope of the curves for N-containing natural polyelectrolytes indicate that they are polyfunctional. The dissociation constants for the active groups are 5.93 (PEI) and 5.25 (PEPA), indicating that the aminated wood is a weak-base anion exchanger ($K_b \approx 10^{-3}$-10^{-5} M, $pK_b = 3$-5) [5, 6] and contains tertiary, secondary, and primary aliphatic amines.

Thus, the results enabled a convenient method to be developed for preparing from wood chemically modified natural ion-exchangers by catalytic hydroxylation of it by diglycidyl ether and subsequent amination of the synthesized α-oxide derivatives with aliphatic polyamines.

EXPERIMENTAL

Wood was activated as before [7].

PEI (Fluka AG) with MW $30 \cdot 10^3$-$40 \cdot 10^3$ and PEPA (Nizhnii-Tagil plant) polymer with MW 365 were stored over granulated KOH and used without further purification.

Wood was alkylated by DGEDHDPP containing 20.97% α-oxidic groups in DMF solution (10%) with or without TEA catalyst of various concentration. Epoxidized samples were etherified and aminated in a three-necked flask equipped with a mechanical stirrer, thermometer, and reflux condenser at 20-100°C. Polymers were solidified in porcelain crucibles in a muffle furnace. Modified derivatives were purified of unreacted substances by extraction with benzene in a Soxhlet apparatus for 5-6 h and dried in a vacuum drying chamber. Their physical chemical properties were determined. The content of epoxides in them was found by reacting them with HCl in acetone [8].

The mass gain of the wood was calculated using the formula

$$(m_{KOH} - m_{init}) \cdot 100/m_{init},$$

where m_{KOH} is the mass of modified sample and m_{init} is mass of initial material.

The equilibrium swelling and amount of titrable N in the polyelectrolytes were estimated as before [9, 10]. Anion-exchangers were prepared for the tests and the properties were determined according to standard methods [9].

Potentiometric titration of ion-exchangers was performed using separate portions and keeping the ion strength constant [5]. The pH of the medium was monitored using a EV-74 universal ion-meter equipped with glass and silver-chloride electrodes. IR spectra of the studied compounds were recorded on a Nicolet 5700 FT-IR spectrophotometer in KBr disks. The compositions of the starting and modified samples were established by elemental analysis.

REFERENCES

1. A. I. Zhyamaitaitis, Author's Abstract of a Doctoral Dissertation in Chemical Sciences, Kaunas Polytechnical Inst., Riga (1990).
2. L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, 2nd Ed., Methuen & Co., London (1958).
3. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 3rd Ed., Wiley, New York (1974).
4. V. V. Korshak, M. I. Shtil′man, A. Kh. Mekhtiev, and A. M. Pomazanova, *Vysokomol. Soedin., Ser. A*, **21**, 1, 42 (1979).
5. K. M. Saldadze and V. D. Kopylova-Valova, *Complexing Ion-Exchangers (Complexites)* [in Russian], Khimiya, Moscow (1980).
6. Yu. Yu. Lur′e, *Handbook of Analytical Chemistry* [in Russian], Goskhimizdat, Moscow (1962).
7. A. V. Obolenskaya, Z. P. El′nitskaya, and A. A. Leonovich, *Laboratory Methods in Wood and Cellulose Chemistry* [in Russian], Lesnaya Promyshlennost′, Moscow (1991).
8. A. I. Toroptseva, K. V. Belogorodskaya, and V. M. Bondarenko, *Laboratory Practicum in the Chemistry and Technology of High-Molecular-Weight Compounds* [in Russian], Khimiya, Leningrad (1972).
9. E. I. Kazantev, V. S. Pakholkov, Z. Yu. Kokoshko, and O. N. Chupakhin, *Ion-Exchange Materials, Their Synthesis and Properties* [in Russian], Urals Polytech. Inst., Sverdlovsk (1966); R. Griessbach, *Austauschadsorption in Theorie und Praxis*, Akademie-Verlag, Berlin (1957).
10. K. M. Saldadze, *Chemically Active Polymers and Their Application* [in Russian], Khimiya, Moscow (1969).