

Reacting Cotton Cellulose with Lignin-Based Polyurethane¹

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ABSTRACT

Chain-extended lignin was reacted with blocked isocyanate and the product, lignin polyurethane (LPU), was subsequently applied by padding to cotton print cloth at three add-on levels: 1.70, 3.45, and 4.30%. Product syntheses and reactivity were followed by FTIR spectroscopy. LPU as a formaldehyde-free finish improved durable press (DP) and dimensional stability of the unfinished cloth, but the improvement was less than conventional amino resin finishes. Unlike conventional resin finishes, LPU showed strength and abrasion resistance retention. Abrasion resistance improved at the 3.5% add-on level. Grafting LPU onto cotton cloth is a surface reaction, given the molecular size of the product and detection by specular reflectance infrared spectroscopy. Even with the limited accessibility of the reactant groups in the unswollen cloth, a sufficient number of carbamoyl linkages formed to improve properties. Although DP ratings were not high, LPUs tailored by alkyloxyhydroxide chain extensions are likely resins for films, nonwoven consolidants, and composite materials, providing receptivity of cellulose to materials for which it has little affinity.

Finishes for Resilient Cotton Cloth

Cotton fabric modified by treatment with a reactant such as the amino resin, dimethylolhydroxyethyleneurea (DMDHEU) to impart freedom from wrinkles and crease retention led to various concepts of permanent press, wrinkle resistance, crease resistance, and durable press [25]. All-cotton permanent press shirts introduced in the late 1950s were unacceptable due to poor abrasion resistance and half-strength retention.

Since the 1950s, alternate approaches to cellulose chemical modification for improved properties involved combination with synthetic polymers through graft copolymerization. These have included crosslinking with monomers such as N-methylolacrylamides [18], arylates [21], acrylamides [22], acrylonitrile [30], vinyl acetate [17], acrolein [26], methacrylic acid [5], etc. These various grafting methods have been described in several reviews [4, 23, 33, 35]. In general, cotton cellulose graft copolymerized fabrics showed

improved and in some cases moderate losses in strength and abrasion resistance and improved wrinkle angle recovery and DP ratings. Copolymerization with pre-, concurrent, or subsequent crosslinking employing DMDHEU showed lower DP than DMDHEU alone, but increased strength and abrasion resistance over the DMDHEU treated cloth [21, 50].

Concurrent with graft copolymerization were chemical modifications by etherification and esterification. These treatments involved permeation of oligomers inside fiber pores to crosslink more hydroxyl groups through rigid three-dimensional networks. Fabric embrittlement and limited durability are tolerable outcomes considering the excellent DP ratings obtained.

Cotton fabric finishing with oligomers has traditionally centered on formaldehyde treatments and formaldehyde's reactions with the active hydrogens on urea and melamine compounds. In conventional amino resins, free or bound formaldehyde is present in finish agents, liquors, and finished fabrics. It can be split off to various extents of hydrolyses with temperature, humidity, time, and resin type. Acids and acid-formers used in processing cause fabric tendering. To solve these problems, workers have investigated various amino resins such as N-methylol compounds of aliphatic or

units. The model lignin structure may be built of 100 monomer units with a molecular weight of 20,000. Lignins isolated by milling and cellulolytic enzymatic action have weight average molecular weights of 15,000 to 20,000 and are linked by alkyl-aryl ether linkages. The reaction of lignin with alkylene oxides affects molecular weight, reduces T_g , and results in more uniform functionality. Molecular weight determinations of hydroxypropylated chain-extended lignins showed a range of number average molecular weights of 1348 to 1951 g/mol [48].

In Figure 1 modified lignins are formed at the phenolic oxygen. Hydroxyethoxylated lignin sulfonated at the alpha-carbon (HELs) was the subject of a previous study. HELs-finished fabric showed less weight loss and improved dimensional stability over DMDHEU-finished cloth but lower DP ratings [8]. Hydroxypropyl lignin (HPL) is formed from the reaction of lignin solids with propylene oxide at the phenolic oxygen site [27, 39]. HPL is precursor to HP/EL, hydroxypropylethoxylated lignin, which is the partially blocked HPL derivative with extended propyl ether chains attached to primary ethyl hydroxide monomer units. HP/EL is the lignin we used in this study. Its primary source is steam-exploded yellow poplar.

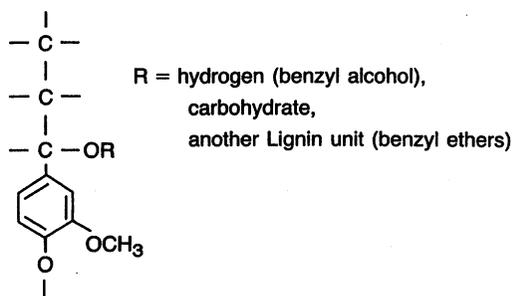


FIGURE 1. Structural model of lignin.

Experimental

MATERIALS

2,4-Tolylene diisocyanate was supplied as pure grade without 2,6 isomer by Mobay Corporation. Pure grade phenol was supplied by Sigma Chemical Company and sublimed for purification. Dibutyltin-dilaurate catalyst was supplied by Union Carbide.

Steam-exploded yellow poplar was obtained from Bio-Regional Energy Associates Ltd., Floyd, Virginia. Propylated and ethoxylated steam-exploded lignin was synthesized and supplied by the Brooks Center, De-

partment of Wood Science and Forest Products, VPI&SU. This synthesis involved reacting propylene oxide with KOH as catalyst, followed by reaction of ethylene oxide to partially cap propylene oxide extensions. The dark viscous product was characterized as 36.3% lignin and 50% homopolymer with a MW of approximately 5000 g/mole. Homopolymer was removed.

The 100% cotton print cloth was a balanced plain weave 80 × 80 count, desized, bleached, and mercerized, 3.2 oz/yd² supplied by Testfabrics, Inc., New Jersey, designation 400M.

METHODS

Synthesis of monocapped, blocked isocyanate, phenyl N-(3-cyanato-4-methylphenyl carbamate) I: At 20°C or less, with equimolar amounts of the reactants, phenol and TDI, there is greater reactivity of the 2-over the 4-position —NCO group in TDI [45]. The reaction was done under nitrogen at ice temperature in a three-neck round bottom flask for dropwise addition of TDI (4-methyl-1,3-phenylene diisocyanate), 154.9 grams, 0.88 moles in anhydrous toluene, to a solution of sublimed phenol (83.2 grams, 0.88 moles) in 200 ml anhydrous toluene. The reaction was continued at room temperature for 24 hours when the product formed. The product was recrystallized from methylene chloride and hexane and then vacuum dried. Melting point was 97°C with yields of 87–92%. The reaction is shown in Figure 2. We verified the identity of the monocapped product by elemental analysis: 66.28% C; 4.63% H; 10.70% N; 16.70% O (C₁₅H₁₂N₂O₃). The IR spectrum of I in Figure 3 shows the pronounced —NCO group absorption at 2261 cm⁻¹ and —NH absorption from carbamoyl nitrogen at 3273 cm⁻¹ with carbamoyl carbonyl at 1730 cm⁻¹.

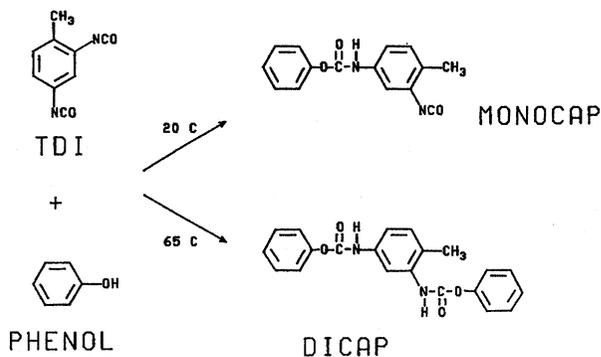


FIGURE 2. Formation reaction of blocked isocyanate (I).

cyclic amides and amino compounds, ureas, carbamates, triazines, and etherified amino derivatives, carbamate, aldehyde, and amidealdehyde adducts, as well as catalysts, application conditions, and cure protocols [1, 10, 40]. From 1984 to 1986, plants had switched from conventional finishes to low formaldehyde glyoxals [15, 16, 55]. At best, strength retention was 50–60%.

More recent developments in formaldehyde-free finishes for cotton cloth have extended early 1960s studies on polycarboxylic acids, which form ester crosslinks with cellulose [7, 43, 44]. Studies of 1,2,3,4-butanetetracarboxylic acid (BTCA) and citric acid (CA) have focused on esterification catalysts based on alkali metal salts of phosphorus-containing acids. Acceptable DP properties and comparable strength retention of 44–66% were found with BTCA, CA, and the other acids, tricarballic and aconitic, which increased resilience but decreased whiteness and abrasion resistance [29, 54, 56].

Applications for Modified Lignins

In this work, we examine derivatized lignin as a formaldehyde-free finish for cotton cloth, considering its feasibility from the following aspects:

Lignin is a biopolymer, renewable biomass, and thermoplastic resin, which is abundantly available. Its use is only a fraction of the 3×10 metric tons contained within the earth's vascular plants [19]. Of this amount, 95% is treated as waste or used as the source of energy in the pulping industry [32].

Lignin products are commercially acceptable. Current products include lignosulfonates for adhesive binders, dye dispersants, yarn size, dust covers, livestock feed, components in phenolic and urea adhesives for plywood and particle board, emulsifiers, sequestering agents, protective colloids to stabilize emulsions, feedstock for the commercial production of vanillin, dimethyl sulfide, and phenolic monomers [31].

Delignification by pulping and subsequent severe changes in lignin have led to a proliferation of reports on lignin structure, properties, modifications, and uses. New materials made from lignin have the same performance levels as petrochemically derived plastics [24, 37, 46].

Lignin has a natural affinity for cellulose; it is found as a distribution between and in the cell walls of cellulosic fibers. It provides a binding and stress-transferring matrix, imparts hydrophobicity and protection from microbiological decay, and acts as an insoluble three-dimensional network or as several networks with differing chemistries and structures.

The chemical reactivity of lignin is defined by the presence of phenol hydroxyl, benzylic hydroxyl, and carbonyl groups. Grafting onto lignin with poly(1-oxy-2-methylprop-1,3-xylene) to add propylene oxide repeat units produces a dark brown viscous liquid polymer derivative containing large numbers of secondary hydroxyl groups. These groups are the principal reactive centers for tailoring reactivities to cellulose. The low reactivity of the secondary hydroxyl groups on these extended alkoxy side arms can be further modified by reaction with ethylene oxide for primary hydroxyl group reactivity. These polyol lignins have been chemically combined with diisocyanates to form urethanes for coatings and adhesives that impart strength and rigidity, resistance to water and solvent, and good bond strength to cellulosic substrates.

Through alkyloxylation, new lignin polymers have been formulated for uniform functionality, increased reactivity, and specific mechanical properties. Particular applications include wood adhesives from hydroxyalkyl lignins with diisocyanate and melamine [39, 47], reinforced fiber mats from the reaction of lignin and hydroxypropylated lignin (HPL) derivatives with diisocyanate in the presence of cellulosic fibers [20], and lignin carbohydrate block copolymers synthesized from the reaction of cellulose triacetate polyurethane and HPL [11]. These modified lignins and their applications suggest the feasibility of tailoring, through syntheses, related lignin derivatives for textile applications involving cellulosic substrates.

Cotton fabrics crosslinked with phenyl isocyanate and the optimum conditions for this reaction have been examined [13]. Crosslinking with phenol isocyanate improves breaking strength and elongation and lowers wrinkle resistance [14, 53]. In another application, the mechanical properties of acetate fibers improve when crosslinked with 2,4-tolylene diisocyanate (TDI) capped with two moles of phenol [2].

In our research, a phenol monocapped (blocked) diisocyanate carbamate was synthesized and reacted with a chain-extended HPL. The product, LPU, was applied to cotton cloth by pad-dry-cure. We examined crosslinking directly from the fabric using specular reflectance FTIR, its effectiveness for improving properties using physical and mechanical fabric testing according to standard AATCC and ASTM procedures, and finish durability using FTIR.

Lignin Model Compounds

Lignin is formed by dehydrogenative polymerization of phenylpropanoid monomers. Thus, lignin can be described by the C9 model phenylpropane monomer

units. The model lignin structure may be built of 100 monomer units with a molecular weight of 20,000. Lignins isolated by milling and cellulolytic enzymatic action have weight average molecular weights of 15,000 to 20,000 and are linked by alkyl-aryl ether linkages. The reaction of lignin with alkylene oxides affects molecular weight, reduces T_g , and results in more uniform functionality. Molecular weight determinations of hydroxypropylated chain-extended lignins showed a range of number average molecular weights of 1348 to 1951 g/mol [48].

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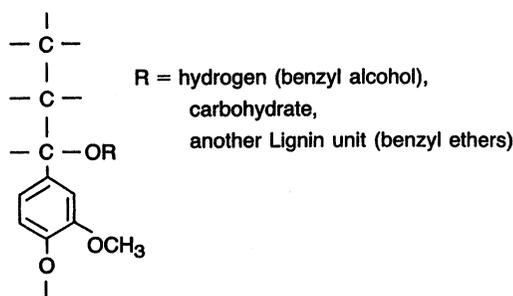


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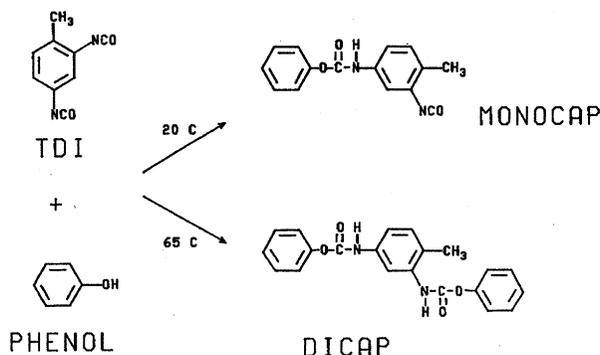


FIGURE 2. Formation reaction of blocked isocyanate (I).

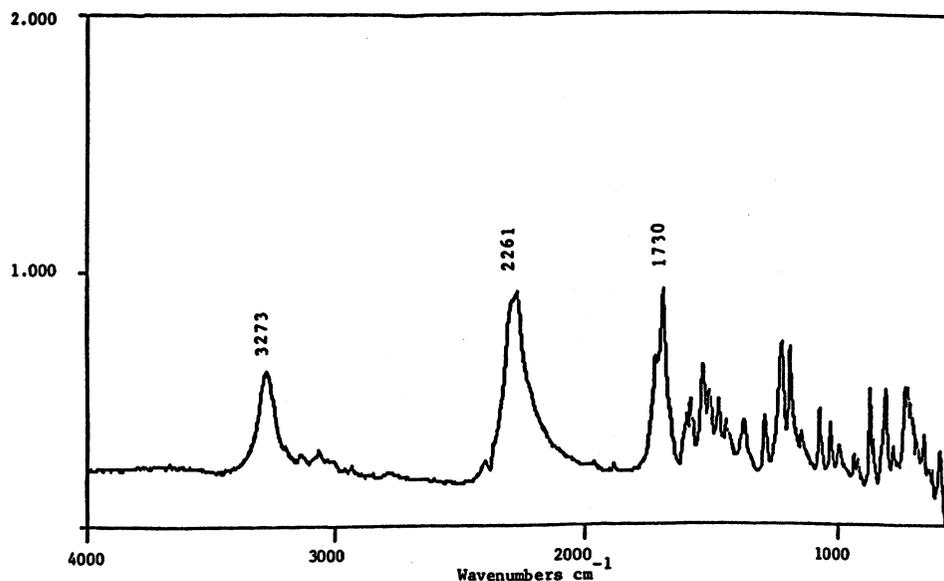


FIGURE 3. Infrared spectrum of blocked isocyanate (I).

Synthesis of lignin-blocked isocyanate copolymer (HP/EL PU): We confirmed a molar ratio of 20 moles blocked isocyanate (I) to 1 mole HP/EL (NCO : OH) by a series of reactions of varying amounts of I to HP/EL of 20:1, 25:1, 30:1, 35:1, and 40:1 shown in Figure 4. In the 20:1 molar ratio, practically all —NCO groups in I are used up. Unreacted —NCO is evident

in the greater mole ratios from the appearance of the 2261 cm^{-1} absorption band.

To a solution of 20 g (0.004 moles) HP/EL in 100 ml methylene chloride and 21.4 g (0.08 moles) I in 100 ml methylene chloride, we added two drops of dibutyltin dilaurate. After reacting 72 hours at room temperature with constant stirring, the product was isolated by rotoevaporation.

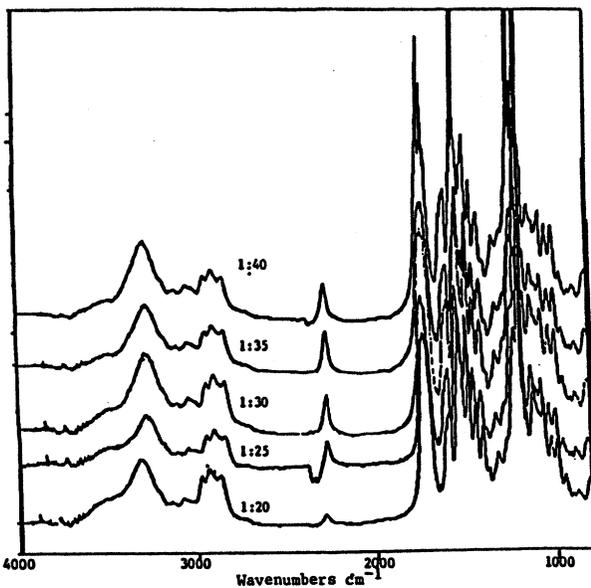


FIGURE 4. Infrared spectra of HP/EL PU at different molar ratios of HP/EL to (I).

CHARACTERIZATION

Determining isocyanate (—NCO) in I: A solution of 0.5 g I in 25 ml methylene chloride was mixed with a solution of 25 ml 0.1N butylamine in chlorobenzene for reaction with —NCO groups. After stirring 15 minutes, 100 ml isopropyl alcohol was added with the indicator, 4–6 drops of bromophenol blue for titration of excess butylamine with 0.1N hydrochloric acid. We calculated the percent —NCO using Equation 1:

$$\% \text{ NCO} = \frac{(B - V)(N \times 4.202)}{\text{weight of sample (g)}} \quad (1)$$

where B = ml 0.1 HCl required for a blank, V = ml 0.1 HCl required for the sample, N = normality of HCl solution, and 4.202 = grams —NCO per equivalent [49].

We determined the percent OH in HP/EL PU by esterification of acetic anhydride and pyridine with back-titration of excess anhydride with standard base using vanillin alcohol as a blank [36]:

$$\% \text{ OH} = \frac{[(t/w w_s)] - t_s(N\text{NaOH}(0.017)(100))}{\text{sample weight in grams}}, \quad (2)$$

where t = ml NaOH for blank, t_s = ml NaOH for sample, w = mg pyridine/acetic anhydride in blank, and w_s = mg pyridine/acetic anhydride in sample.

Characterization of the reactants I and HP/EL for HP/EL PU formation can be found in Table I, which shows that the HP/EL polymer contains five star-like macromers with radiating arms and a MW of 5000 g/mole. Each macromer contains 5-C9 units, and each unit is chain-extended with one OH group at the end of each chain extension. Because the MW is an average value, it allows for a reactivity of 20 to 25 OH groups on HP/EL with I. Thus an approximate MW for the finish HP/EL PU would include 20 units of I, that is, 20 (268) g/mole I + 5000 g/mole HP/EL = 10,360 g/mole HP/EL PU [41].

TABLE I. Characterization of reactants.

Reactant	Parameter	Value
HP/EL	no. avg. MW	5000
HP/EL	OH number ^a	230
HP/EL	% OH groups	6.9
HP/EL	no. OH groups/mole	20.5
I	MW	268
I	% NCO groups	15.67
I	no. NCO groups/mole	1.0

^a Number milliweights of KOH per unit weight that is chemically equivalent to the active functions per unit weight of the compound.

We determined the nitrogen content in HP/EL PU for each of the reaction molar ratios of I (NCO) to HP/EL (OH) in Table II. Figure 5 shows one C9 unit of HP/EL PU crosslinked to cellulose.

Experimental

For the pad-dry-cure procedure, a padding mangle was used to apply HP/EL PU dissolved in methylene

TABLE II. Nitrogen content in HP/EL PU finish.

Molar ratio NCO/OH	Actual %N ^a	Theoretical %N ^b
20:1	5.24	4.60
25:1	5.58	5.40
30:1	5.91	5.98
35:1	6.84	6.81
40:1	7.04	7.12

^a Determined by independent commercial laboratory. ^b Determined from Equation 3:

$$\% \text{ N} = \frac{28 \times n}{5000 + (268 \times n)} \quad (3)$$

where n is the number of moles of blocked isocyanate I, that is, when $n = 20$, % N = 5.4%.

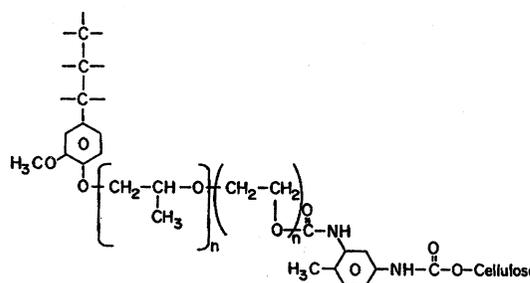


FIGURE 5. HP/EL PU crosslinked to cellulose.

chloride by one dip and one nip to three different levels of theoretical add-on, 1, 3, and 6%, as calculated by the numbers in Table III. Fabrics were tentered on pin frames and air-dried, followed by curing at 160°C for 5 minutes. At 130°C, the phenol cap is labile and cellulose crosslinks to HP/EL PU at these reactive sites.

ANALYSIS OF FINISHED FABRICS

We determined nitrogen content of HP/EL by the Kjeldahl method for calculating percent add-on using Equation 4:

TABLE III. HP/EL PU finish bath compositions.

	Theoretical add-on ^a					
	1%		3%		6%	
	%	amount, g	%	amount, g	%	amount, g
Methylene chloride	98.4	374	95.3	362	90.6	453
HP/EL PU	1.56	5.9	4.68	17.7	9.38	35.6

^a Theoretical add-on is based on 64% wet pickup and 380 g total weight of fabric.

$$\% \text{ Add-on} = \frac{\% \text{ nitrogen in the fabric}}{\% \text{ nitrogen in HP/EL PU}} \quad (4)$$

where % nitrogen in HP/EL PU was 5.4% from Table II. Nitrogen contents of the finished fabrics were determined by the Kjeldahl method before and after five wash/dry cycles. Table IV summarizes the results and shows finish loss, possibly from the fabric surface, at all add-on levels.

Dimensional changes were measured by AATCC test method 135-1987, wrinkle recovery by AATCC 66-1984, durable press by AATCC 124-1984, tensile strength (grab method) by ASTM test method D 1682-64, and abrasion resistance (Stoll-Flex) by D3885-80.

EVIDENCE OF GRAFTING

We used specular reflectance infrared spectroscopy to analyze the surface of the finished fabrics for evidence of finish adhesion and durability. We have reported previously on this spectroscopic technique [9]. Figure 6 shows HP/EL PU-finished fabric before and after curing. The principal differences in these spectra lie within the 1500 to 1750 cm^{-1} absorption region. In the difference spectra, Figure 7, of cured minus uncured fabrics from Figure 6, we used scale factoring to flatten both sides of this absorption region. Figure 7 shows

the presence of bands at 1724 cm^{-1} for urethane carbonyl [42], 1598 cm^{-1} for the —C=C— vibration of aromatic lignin and TDI [12, 38], and 1533 cm^{-1} for —NH deformation from amide carbamoyl [34], which are present only in the HP/EL PU cured fabric.

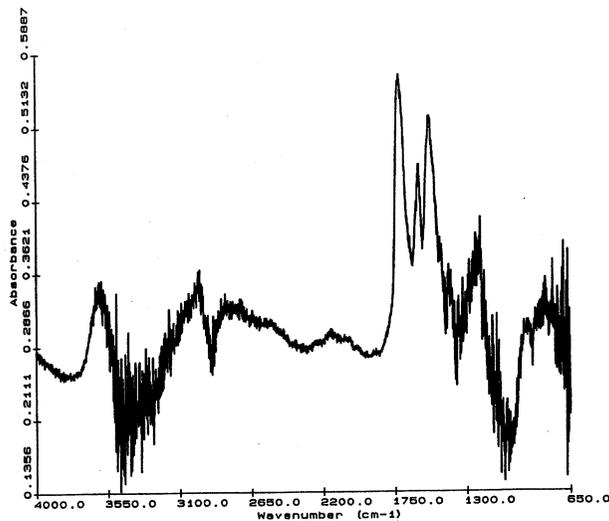


FIGURE 7. Specular reflectance difference spectrum of HP/EL PU cured minus uncured cotton print after extraction.

TABLE IV. Nitrogen content in HP/EL PU-finished fabrics.

Theoretical add-on	%N before 5 wash/dry cycles	% Add-on before 5 wash/dry cycles	%N after 5 wash/dry cycles	% Add-on after 5 wash/dry cycles
1%	0.118 ± 0.002	2.1	0.096 ± 0.001	1.7
3%	0.206 ± 0.003	3.7	0.193 ± 0.003	3.5
6%	0.272 ± 0.004	4.9	0.241 ± 0.003	4.3

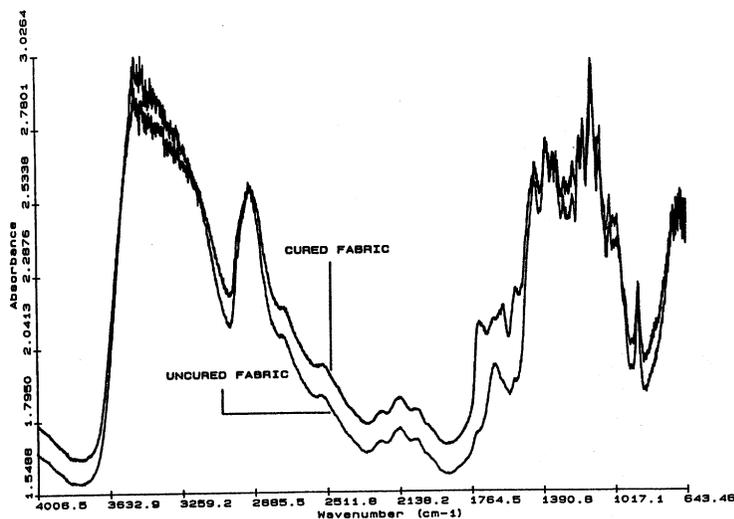


FIGURE 6. Spectular reflectance IR spectra of HP/EL PU cured and uncured cotton print cloth.

We evaluated the durability of the finish using IR spectra of finished cured fabrics after Soxhlet extraction from methylene chloride at its reflux temperature for 48 hours. Figure 8 shows the spectra of fabric before and after extraction with the same infrared absorption bands, indicating the LPU finish is durable to extraction by the solvent in which the LPU was dissolved and from which it was applied to the cloth.

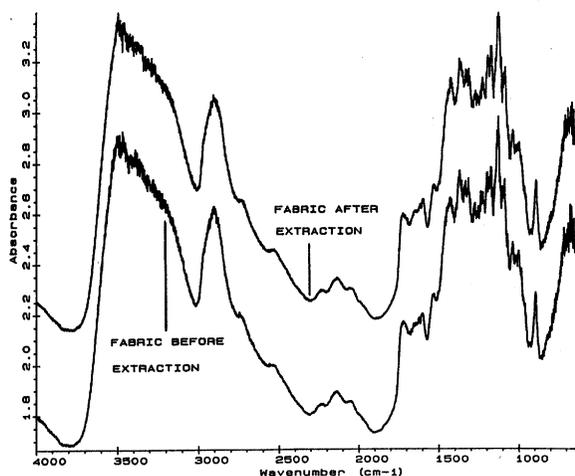


FIGURE 8. Specular reflectance IR spectra of HP/EL PU finished fabrics before and after extraction.

When yarns from the finished fabric were withdrawn, untwisted, and pulled apart to expose fiber ends, these ends in the scanning electron micrographs of Figure 9 appear to have some loss of fibrillar structure. They appear partially fused and swollen, indicating possible grafting of LPU to cellulose.

Results and Discussion

There is evidence of the possibility of surface grafting chain-extended ethoxylated hydroxypropyl lignin

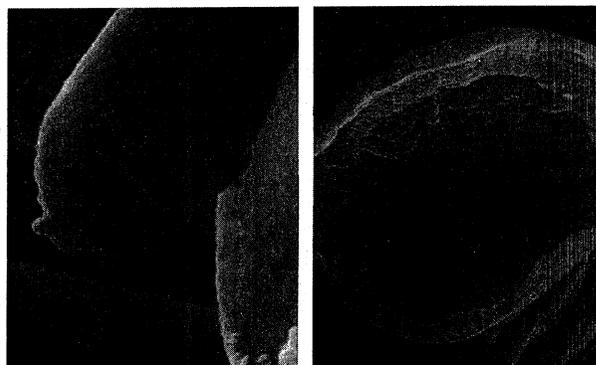


FIGURE 9. Fiber end, LPU-treated, 6400X (left) and fiber cross section, LPU-treated, 12,500X (right).

blocked isocyanate, HP/EL PU, with cellulose polymers in cotton fabric through carbamoyl linkages. Cellulose can react chemically as a trihydric alcohol with limited accessibility of hydroxyl groups, due in part to its high crystallinity. Chemical reactivity would be somewhat limited to the accessible amorphous regions. The fabrics were crosslinked in the unswollen state, which can contribute to nonuniform distribution. Nonetheless, with limited and uneven reactivity, enough reactivity occurred to change certain measured physical and mechanical parameters.

We compared dimensional stability, wrinkle recovery angle, durable press ratings, tensile strength, and abrasion resistance of fabrics finished with HP/EL PU at 1.7, 3.5, and 4.3% add-on to untreated control fabrics. Table V gives the results compared to citric acid (CA) finished fabric. Statistical analysis was applied by paired comparisons between means using a *t* test, and significant differences are reported at the 95% level of confidence. HP/EL PU showed a significant improvement in DP ratings at all levels of add-on when compared to the unfinished cloth, but no significant differences in the three add-on levels. Wrinkle recovery

TABLE V. Fabric properties from HP/EL PU finish and reported CA finish.^a

Finish	Add-on	Durable press rating	Wrinkle recovery angle, $w + f$, °	Breaking strength (warp), lb	Stoll flex cycles (warp)
HP/EL PU	1.7%	2.6	172	62	260
	3.5	2.7	175	54	270
	4.3	2.2	133	48	298
Untreated (after 5 wash/dry cycles)	0.0	1.6	191	52	260
	5% CA ^a	3.5	256	34	148
Untreated ^a	0.0	1.0	194	56	234

^a Reference 28.

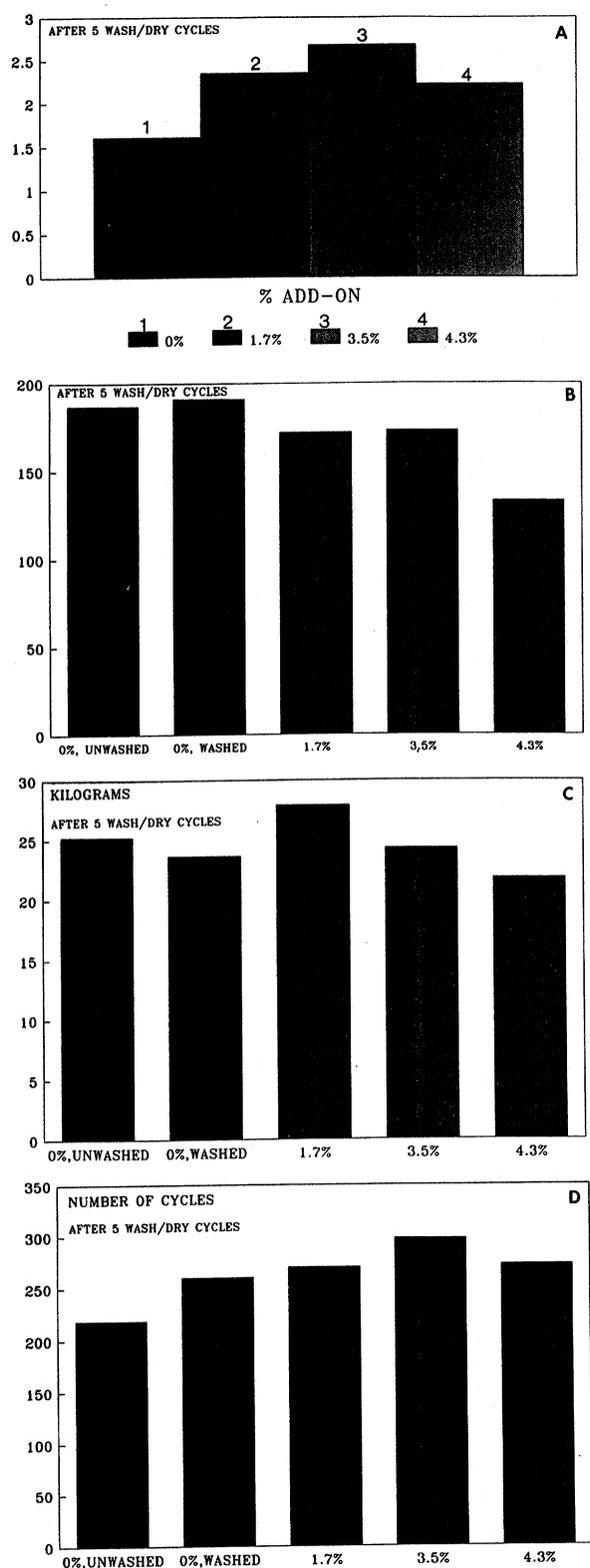


FIGURE 10. Fabric parameters after five wash/dry cycles: (A) durable press ratings, (B) recovery angle (warp and fill), (C) tensile strength, and (D) abrasion resistance.

angle was not significantly changed from the unfinished cloth at 1.7 and 3.5% add-on, but it was significantly less at the 4.3% add-on level. An important contribution of HP/EL PU finish is strength retention. At all levels of add-on, there were no significant changes in breaking strength when compared to the unfinished fabrics. Another important contribution of this finish is retention of abrasion resistance at 1.7 and 4.3% and a significant increase at 3.5%. These parameters are depicted in Figure 10, A-D.

In Figure 11, we measured dimensional stability, an indication of shrinkage, or the ability of the fabric to return to its original dimensions after laundering, in the warp and weft directions. More shrinkage is expected in the weft, which usually has yarns of fewer twists per inch and can thus swell more effectively to take up a smaller volume. Weft and warp shrinkage were significantly less, 6.3 to 8.4% for all HP/EL PU-finished fabrics, when compared to the unfinished control fabrics with 13.8% weft shrinkage. Even with this improvement, however, shrinkage in HP EL/PU-finished fabrics is still appreciable.

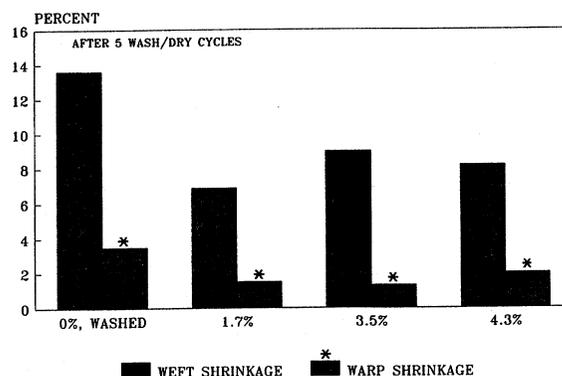


FIGURE 11. Dimensional stability of unfinished and finished fabrics.

Conclusions

Lignin polyurethanes can be tailored through chain extensions over a broad range of glass transition temperatures where hard aryl segments are combined with soft alkoxy segments. Modified chain-extended lignins can react with cotton by grafting through carbamoyl linkages. The length of the chain extensions can affect the flexibility of cellulose polymer chains and modify fabric properties. For example, long and mobile extensions would result in lower DP ratings when cellulose chains were given greater freedom of movement. Long extensions should, however, contribute to a softer fabric hand. There is room for further investigation to tailor

a different LPU for more improved DP properties than HP/EL PU.

The most striking difference with HP/EL PU compared to the conventional DMDHEU resins and polycarboxylic acids is that the LPU finish does not lower fabric strength or abrasion resistance and moderately controls shrinkage. This could have resulted from grafting alone or grafting accompanied by adhesion of self-associated resin. These results suggest other uses for products from the chemical combination of LPU and cellulose, for example, consolidants and thermoplasts for molding, which incorporate cellulose with materials for which it has little or no reactivity.

A drawback to using lignin as a fabric finish is the color it imparts, but this problem can be solved. Alkoxylated lignins lose 95% of their color in oxidation or reduction bleaching [19]. Other information exists on the nondegradative bleaching of lignin [3, 51, 52]. Another drawback of the system is the toxic terminated-phenol capped isocyanate prepolymer. A keto oxime such as propane oxime, butanone oxime, or benzophenone oxime, which is labile at cure temperature, can be substituted for phenol [6]. Still another drawback of the system is processing from an organic solvent medium; this problem can be solved by sulfonation. The possibility of yellowness developing can be examined by aging studies. Yellowing can arise from the light absorption properties of the aromatic rings in LPU, from both lignin and TDI moieties. Although aliphatic diisocyanates have greater light stability of the derived polyurethanes than aromatic diisocyanates, they have limited use because they are slower reacting and lack the greater selectivity of one —NCO group over the other. Color reduction and reversal can be examined. With the possibility of crosslinking lignin-based polyurethane to cellulose in cotton cloth, these problems now merit investigation. The increasingly broad range of reactivities and uses of cellulose and associated biomass suggests possibilities for new textile products and applications.

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