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Publisher's version / Version de l'éditeur:

[Proceedings of the Conference], 2016-09-26

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Modified Lignin as Main Composition for New Generation of Polyurethane Rigid Foams

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ABSTRACT

This research aims at improving the integration of lignin in polyurethane (PU) rigid foams. First, lignin was chemically modified to introduce amine groups on its molecule. The purpose of this step is to enhance the lignin direct reactivity with isocyanate to form urea bonds and also to use this modified lignin as a catalyst for the main reaction involving polyol and isocyanate. A simple one-step approach, without toxic solvent, was used for this modification. The efficiency of this modification was verified using Fourier transform infrared spectroscopy (FTIR), electron dispersion X-ray (EDX) and scanning electron microscopy (SEM). Then, the resulting modified lignin was incorporated at 10 and 20 wt % in the formulation of PU rigid foams. The influence of lignin on foaming ability was also evaluated. In addition, the effect of modified lignin on mechanical properties, thermal conductivity and density of the foam was also investigated.

KEYWORD: Polyurethane rigid foams, lignin, chemical modification, characterization, foaming

INTRODUCTION

A number of chemicals involved in the mass production of commonly used polymers are suspected to be responsible for major health issues and/or to have negative environmental impacts. Their regulations are under serious revision, especially by government legislation and new environmental policies [1-4]. In this context, spray PU rigid foam widely used for insulation have been the subject of concern due to the utilization of isocyanate and other chemicals [5]. In addition, one of the greatest environmental challenges faced today by the industry is the global climate change partially due to a significant increase in the fossil resources consumption. Increasing the level of carbon dioxide in the atmosphere is causing a climate modification affecting not only the environment but also the human health and economy. Replacing petroleum-based chemicals involved in mass production by renewable bio-based ones is one among the most effective ways to reduce those impacts.

The North American industry produces 9 million tons/year of PUs, containing in average 40% in weight of diisocyanates. PU is synthesized by the reaction between a polyol and an isocyanate, forming urethane linkages as the main structure of the thermoset network (Figure 1). The diisocyanates usually involved are methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), representing respectively 61.3% and 34.1% of the market. For the polyols, they can be divided in two families: the polyester and the polyether polyols. Both are generally synthesized from fossil resources, making their price sensitive, and their negative environmental impact is substantial. In this context, the PU industry needs solutions to produce greener products. Among the multitude of resources extracted from biomass, vegetable oils and lignocellulosic components have a great potential, notably to design monomers (mainly polyols) for the synthesis of bio-based PUs.

Lignin, a byproduct from pulping mills, represents, after cellulose, the second most abundant biopolymer on earth. Today it is mainly burnt to provide energy to the mills. Its production consumes low energy (12 MJ/kg) and does not emit but consumes CO₂ (0.22 kg CO₂/kg lignin) for acidifying black liquor. Lignin is a biopolymer containing high levels of hydroxyl groups in its backbone (both aliphatic and aromatic), methoxyl, carboxyl, and carbonyl moieties in different amounts, depending on the type of biomass and extraction method employed. Lignin is insoluble or has limited solubility in most organic solvents, making its handling difficult for most of the synthesis processes. Specific modification of lignin is an effective strategy to facilitate its integration into polymer materials and more specifically, to make it more compatible with polyols [6, 7]. Currently, the approaches for lignin utilization in polymer products include its use as filler or as macro-monomer in the phenol-formaldehyde and epoxy resins or in PU formulation [8, 9]. The best approach to produce lignin based PU should be a direct modification of lignin molecule in order to improve its reactivity with isocyanates.

The objective of this project was to develop PU rigid foams with a high content of renewable resources. To improve the dispersion of lignin particles in polyol and their reactivity with isocyanate, surface modification with 3-aminopropylsilane (APTES) was performed in order to graft amine functional groups on the particle surface. The resulting lignin powder was directly used in the formulation of rigid PU foams. Figure 2 summarizes the pathway of the approach.

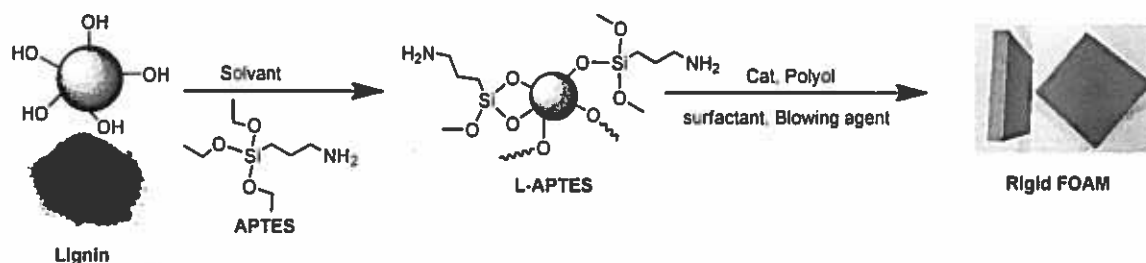


Figure 2: Reaction pathway of the chemical modification of lignin and resulting PU rigid foam.

EXPERIMENTAL

Materials

All reagents were used as received without purification. The lignins used in this study are Indulin AT from MeadWestvaco and a lignin precipitated from Kraft black liquor denominated in this study (PKL). 3-

Aminopropyltriethoxysilane 99% (APTES) was supplied from Sigma-Aldrich. Dimethylcyclohexane amine 99% (DMCHA), Jeffcat ZF-22, Jeffcat TD-33A, Jeffamine D400 and methylene diphenyl 4,4'-diisocyanate based isocyanate (MDI) were obtained from Huntsman. Other chemicals include Tegostab B8484 and Tegostab B4113 from Evonik Industries, DABCO-K15 from Air Product, and Stepanol PS2412 polyol from Stepan.

Characterization

FTIR

Data acquisition was directly performed in solid state, using a Golden Gate ATR probe SPECAC instrument. Spectra were collected by a Thermo Nicolet iS50R FT-IR spectrometer, operating in the attenuated total reflection (ATR) mode (Smart Performer, ZnSe crystal). The scan parameters were: 64 scan, 4000–400 cm^{-1} at a resolution of 4 cm^{-1} . The spectra baselines were corrected manually. Spectra analysis was performed using the OMNIC software.

Thermal conductivity

The thermal conductivity of the foams was measured using a LaserComp heat flow meter instrument from LaserComp Inc. controlled by the WinthermV3 acquisition software. The dimensions of the tested samples were 1''x6''x6''. Two samples were tested for each formulation.

Density and open cells measurement

The density of the foams was determined according to ASTM D1622. Samples of determined dimensions (0.78''/0.78'' on the square base and 1.26'' in the rising direction) were weighted. Density was calculated as ratio of mass per unit of volume (kg/m^3). The open cells ratio of the foams was determined using a model-1 pycnometer from HimiPyc™ controlled by InstruQuest Inc. acquisition software. Helium was used as flow gas. Experiments were carried out according to ASTM D6226-05. Two samples were tested per formulation.

SEM and EDX

SEM micrographs were obtained using a Hitachi scanning electron microscope (S 2600 N, Tokyo, Japan) operating in high-vacuum mode at acceleration voltages of 2-16 kV. A 30-50 nm thin layer of Pd/Au was deposited using a Cressington Sputter Coater, model 108, on the samples prior to SEM analysis to minimize the charge effect due to the insulating properties of the samples. EDX was performed directly in the SEM using the beam as X-Ray source and a dedicated detector for the energy discrimination.

Lignin grafting with APTES

APTES was used to modify the lignin. APTES was mixed with MeOH/H₂O mixture in (95/10 %vol) and the resulting solution was kept 30 min under agitation to allow the hydrolysis of the silane groups. 10 g of lignin was added slowly under rigorous agitation. After 3 h of reaction at room temperature, the suspension was filtered and the remaining solid was washed three times with distilled water. The functionalized lignin was then dried in an air oven at 60 °C before being characterized by FTIR spectroscopy.

PU rigid foams preparation

All rigid foams were prepared using the polyol generic formulation presented in Table 1. The samples were produced by casting the foam in conical paper cups. First, the polyol was mixed with the catalysts, the surfactant, the physical blowing agent and the water for ~5-10 min at 1500 rpm using mechanical stirring. Then, the polymeric MDI was

added at the same stirring speed for 10 seconds. The foaming velocity, height, volume and temperature were recorded using a FOAMAT system from Format Messtechnik GmbH. Foaming recording was performed directly in the cup. For the lignin foams, lignins were blended with the polyol mixture mentioned about (representing 10 or 20 wt % in the polyol) prior to the addition of the isocyanate. In every formulation, the isocyanate index was fixed at NCO/OH=1.6 based on polyol's OH index.

Table 1: Formulation of the rigid foam

Chemicals	(wt%)
Stepanpol 2412	100
Surfactant Tegostab B-8484	3.5
Catalyst JEFFCAT DMCHA	0.56
DABCO-K15	1.7
Water	2.80
Polyol 365 MFC	12.71
Lignin	10-20

RESULTS AND DISCUSSION

Modification of lignin

Amine groups were grafted on the lignin backbone to increase the reactivity of the lignin particles during the foaming and gelling reactions of the PU. Various reactions involved in the PU rigid foams synthesis are summarized in Figure 2. Amine groups can react much faster with isocyanate groups than with hydroxyl groups in the lignin backbone to form urea linkage. Functional groups in the lignin molecules are mainly phenolic hydroxyls, aliphatic hydroxyls and carboxyl aryl ethers. Among them, hydroxyl groups were selected to be the main site of the modification with silane because they are not easily involved in the chemical reactions to form PU foams. Chemical modification of the lignin with APTES should bring two advantages: a slight reduction in the lignin polarity (facilitating the dispersion of lignin in polyol phase) and an improved reactivity of the lignin surface with isocyanate (via urea reaction).

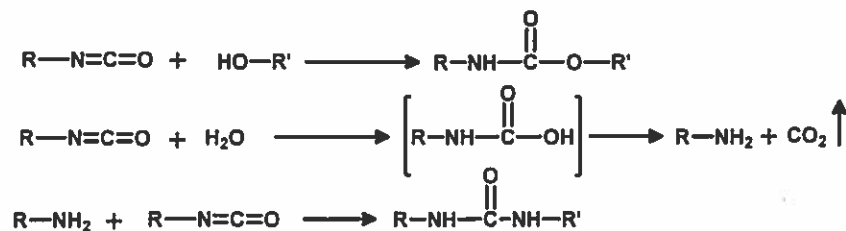


Figure 2: Main reactions involved in the polyurethane foams production.

According to the literature, in presence of water, alkoxy groups can be hydrolyzed leading to the formation of silanols. Therefore, the silanols can react with hydroxyl groups on the surface of the lignin to form covalent stable bonds [10-

12]. Figure 4 presents the FTIR spectra of modified and unmodified lignin. The reaction of the APTES with lignin is confirmed by the appearance of an absorbance band at 1080cm^{-1} (Si-C groups) and the diminution the lignin hydroxyls band at $3200\text{-}3500\text{ cm}^{-1}$ and the appearance of the peak of bonded NH and NH_2 at $3287\text{-}3353\text{cm}^{-1}$. The Ar-O-Si formation was confirmed by the little shift of the 1594 cm^{-1} band to 1589 cm^{-1} (aromatic hydroxyl transformed into aromatic silicon) [13].

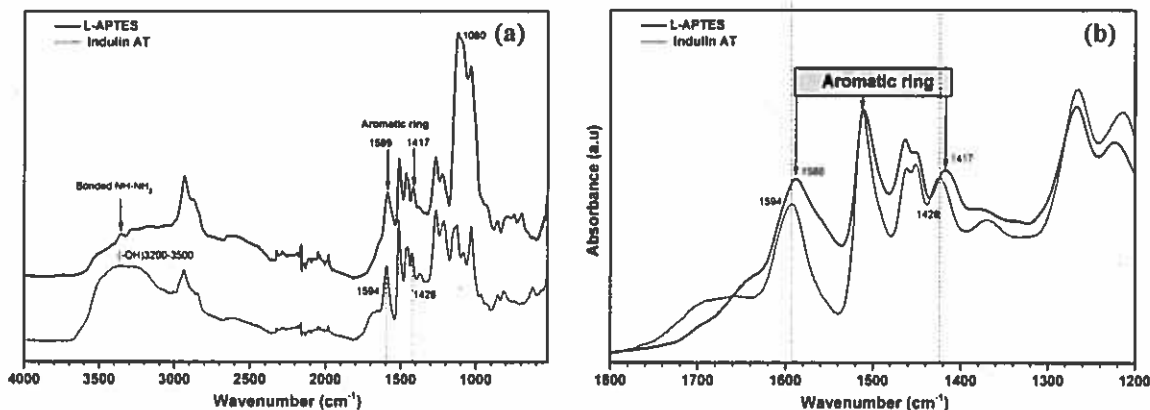
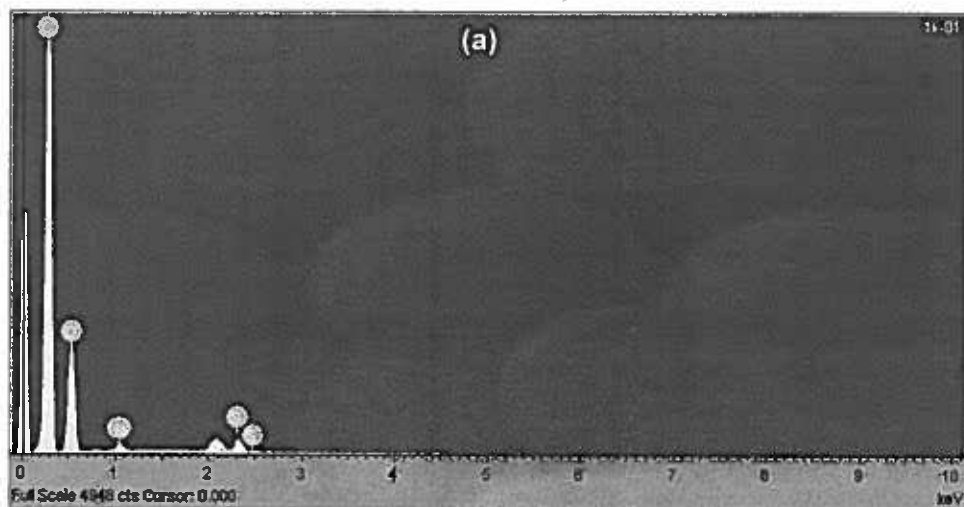


Figure 3: Infrared spectra of: (a) lignin grafted APTES and Indulin AT lignin, (b) extended region.

In order to confirm the reaction between APTES and the hydroxyls of the lignin, EDX was performed. The results are presented in Figure 5. The EDX spectrum exhibits a clean characteristic X-ray emission peak of the silicone element confirming the presence of the APTES on the lignin surface. The micrographs show that the treatment completely modified the morphology of the lignin particle, which switched from big aggregates to finer particles. This should allow a better dispersion of the lignin in the polyol and provide more surface area for the reaction. Similar modification was performed in the case of PKL lignin and similar results were obtained, which are not shown here.



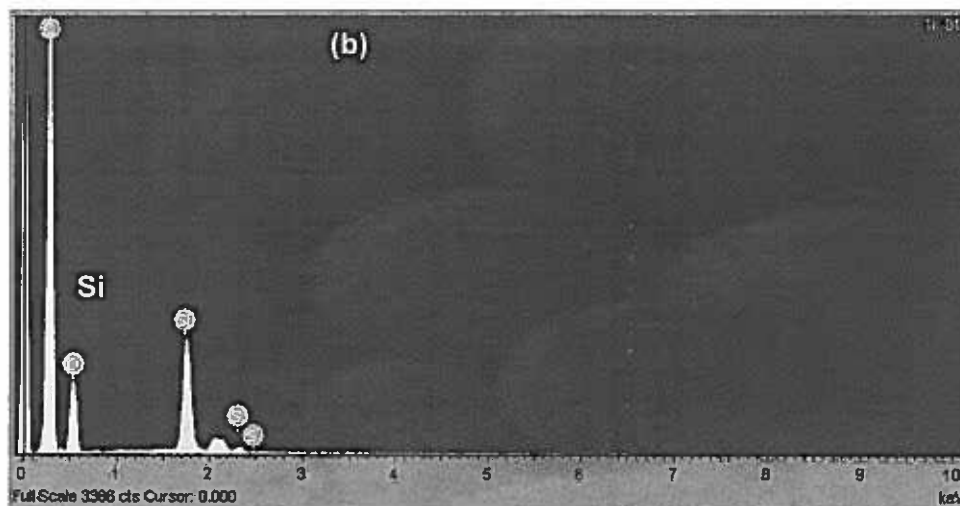


Figure 5: EDX spectrum of: (a) unmodified lignin Indulin AT, (b) modified lignin

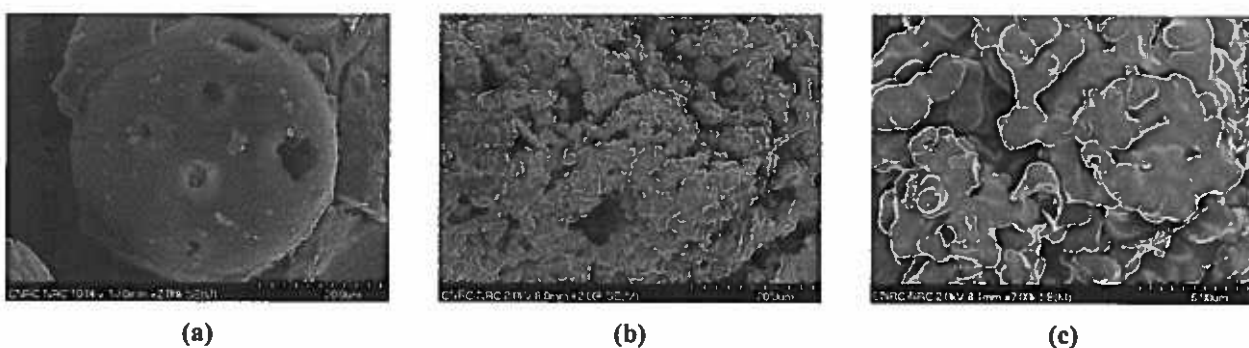


Figure 6: SEM micrographs of the surface of Indulin AT prior the chemical modification (a) and after (b, c).

Table 2 contains a summary of the foaming characteristics of the PU foams obtained from Foamate measurements. A reference sample, containing no lignin, was also produced for comparison. For each lignin foam, two concentrations were used, 10 and 20 wt% in the polyol. Both Indulin AT and PKL lignins with and without modification were used. As shown in Table 2, unmodified lignin systematically slows down the foaming and also reduces the final height of the foam. The negative impact on the reactivity can be explained by two factors. First, unmodified lignin increases the viscosity of the mixture, making it more difficult for the gas cavity to form and grow efficiently. Second, it can absorb some of the additives of the polyol mix, especially water, due to its hydrophilicity. These alter the balance in the formulation hence reducing the foaming ability.

Modification of lignin by silylation with APTES alters the lignin particle granulometry and the surface chemistry as demonstrated above (Figure 6). Smaller particles have less impact on foam formulation and the improved interface with the polyol could slow down phase separation. On the other hand, the presence of amine groups on the surface of the lignin particles may help to catalyze the foaming reaction, since primary, secondary and tertiary amines are known to be efficient catalysts in the PU chemistry. Thus, it is not surprising that the modified lignins have less negative impact on the foaming process as compared with unmodified lignins, especially for PKL (Table 2).

Table 2: Foaming characteristics of the foam samples

Lignin (%)	Max velocity (mm/s)	Max height (mm)	Final height (mm)
0	6.7	154	153
Indulin AT			
10	3.4	124	124
20	3.0	121	120
Modified Indulin AT			
10	4.1	137	136
20	4.5	142	142
PKL			
10	3.7	135	134
20	1.6	120	120
Modified PKL			
10	4.7	141	141
20	3.8	139	139

The physical properties of foams do not only depend on the density and/or rigidity of the polymer matrix, but are also related to the morphology of cells. Usually, rigid PU foams used for thermal insulation contain mainly closed cells. The properties of such foams are significantly affected by the cell size, cell size distribution and cell shape. Usually, irregular and open cells lead to higher thermal conductivity which is not desirable. Figure 6 shows SEM cross-section of samples containing no lignin, unmodified lignin and modified lignin. The reference foam shows a regular distribution of the cells with an average cell size of 400 μm . The introduction of unmodified lignin in the foam clearly changes the morphology. The average cell size tends to decrease but the disparity tends to increase. A few very large cells are visible. This comes from two factors. First, lignin behaves as a nucleating agent, promoting the growth of early cells which have more time to grow. Second, some lignin particles, not involved at all in the crosslinking process, are trapped in the cells walls. As a result, they destroy the cell walls especially when their size is greater than cell wall thickness, leading to anarchic coalescence. With the incorporation of modified lignin, cellular shape becomes smaller, but stays more homogeneous and regular. The average cell size is 250 μm . This regularity shows that lignin particles do not break the walls anymore, most likely because they are directly involved in the three dimensional network. The rigid foams produced with modified lignin have good dimensional stability. In terms of open cells, rigid foams for thermal insulation are expected to stay below 10%. All foams produced with or without lignin comprise less than 8% open cells (Table 3).

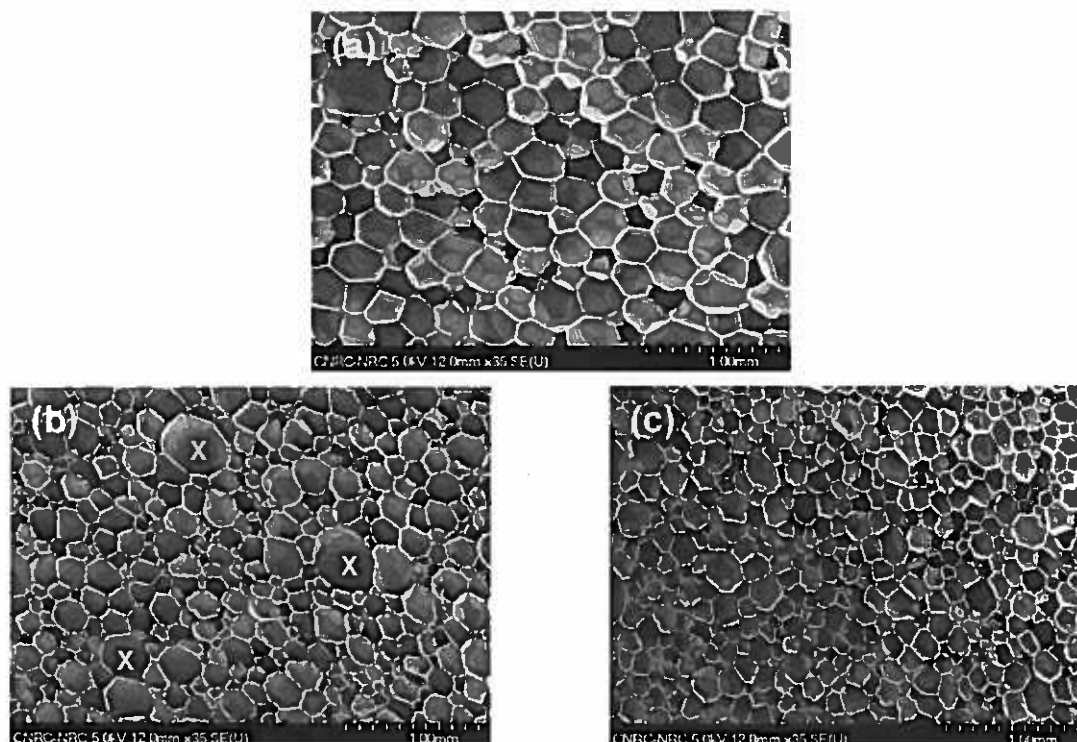


Figure 6: SEM micrographs rigid foams: (a) reference sample without lignin, (b) 20 wt% unmodified PKL, (c) 20 wt% modified PKL.

Table 3 summarizes the main physical properties of the foams, including density, thermal conductivity and open cells content. The density of rigid foams for thermal insulation is generally comprised between 30 and 100 kg/m³ depending on the final application. For example, foams with a density of 30 kg/m³ have typical values R (inverse of the K factor or conductivity) in the range of 40 to 60 mK/W [14]. The properties obtained for all rigid foams formulated without and with lignin are in the expected ranges with density between 30 and 40 kg/m³ and R values lower than 40 mK/W.

Table 3: Properties of rigid foams

Lignin %	Conductivity (kW/mK)	R mK/W	Open Cells (%)	d (kg/m ³)	Modulus at 10% strain (MPa)	Stress at 10% strain (MPa)
0	25.6 (0.2)	39	6.0 (0.7)	36	8.55 (0.75)	0.285 (0.01)
PKL						
10	24.2 (0.3)	41	4.4 (0.7)	36	9.66 (0.70)	0.275 (0.01)
20	24.9 (0.4)	40	5.3 (1.0)	40	6.20 (0.42)	0.189 (0.01)
Modified PKL						
10	24.4 (0.2)	41	7.5 (1.3)	31	6.17 (0.80)	0.200 (0.01)
20	25.2 (0.2)	40	6.6 (1.9)	34	6.20 (0.42)	0.238 (0.01)

Mechanical properties

The compression properties of the foams containing lignin tends to slightly drop compared to those of the reference, especially at high lignin content of 20% (Table 3). The drop in compression properties for the foam with 20% unmodified lignin probably is due to the defects introduced by the lignin particles in the structure as discussed earlier. The drop in compression properties for the foam with modified lignin is likely due to a reduction in density as compared to the reference foam. If the density is taken into account, the specific compression properties (i.e. compression properties/density ratio) of these foams are equivalent to those of the reference foam. This demonstrates the advantage of the modified lignin as compared to unmodified lignin.

CONCLUSIONS

This work presents a simple but efficient way to modify the surface chemistry of commercial lignin particles using silane/hydroxyl reaction. The completion of this reaction was confirmed using various analytical techniques. This modification improves the reactivity of the lignin for its application in PU rigid foams without having negative impact on the foaming properties and cellular structure. The lignin does not behave as a simple filler in the foam but rather participates in the PU crosslinking network reaction. This inclusion tends to homogenize the structure of the foam and to provide the good properties. Those modified lignins might also be considered for use in other types of chemistry, such as non-isocyanate PU (reaction with cyclocarbonate) or epoxy resins.

Acknowledgment: The authors acknowledge the financial contribution from NRCan's PERD program for the project 3C01-001 NN35.

BIOGRAPHIES



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