CELLULOSE CHEMISTRY AND TECHNOLOGY

INVESTIGATION OF STRUCTURAL AND THERMAL PROPERTIES OF DIFFERENT WOOD SPECIES TREATED WITH TOLUENE-2,4-DIISOCYANATE

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A chemical reaction between some reactive compound of different wood species and a chemical reagent, without catalyst, to form a covalent bond between them was performed in the present study. Wood samples of a softwood species, namely spruce (*Picea abies*), and a hardwood one, eucalyptus (*Eucalyptus globulus*), were treated with toluene-2,4-diisocyanate (TDI) at 60 °C, for 1.5 h. Structural changes in wood structure were evidenced by means of Fourier Transform infrared spectroscopy (FTIR). Spectra data gave good evidence for the formation of carbamate ester (urethane bonds) in the treated wood, with some differences related to the wood species. The thermal behavior of untreated and treated wood was also evaluated.

Keywords: softwood, hardwood, toluene-2,4-diisocyanate (TDI), FTIR analysis, TG-DTG-DSC analysis

INTRODUCTION

Lignocellulosic materials, such as wood, are generally sold as high-volume, low-performance products. Lignocellulosic fibers have a three-dimensional structure and are composed mainly of cellulose, hemicelluloses and lignin, with minor amounts of protein, extractives and inorganic substances. Lignocellulosic materials change dimensions with changing moisture content, because the cell wall polymers contain hydroxyl and other oxygen-containing groups that attract moisture through hydrogen bonding.[1] Hemicelluloses are mainly responsible for moisture sorption, but the accessible cellulose, non-crystalline cellulose, lignin and the surface of crystalline cellulose also have a role to play.

Under outdoor conditions lignocellulosic resources undergo photo-chemical degradation caused by ultraviolet radiation. This degradation takes place primarily in the lignin component, which is responsible for the characteristic color changes.[2] The surface becomes richer in carbohydrate polymers as the lignin degrades.

Wood properties, such as dimensional instability, flammability, biodegradability and degradation caused by acids, bases and ultraviolet radiation, are all a result of chemical reactions, which can be prevented or, at least, slowed down, if the cell wall chemistry is altered.[3-6]

Many chemicals have been used, including anhydrides, acid chlorides, ketene, carboxylic acids, isocyanates, aldehydes, acrylonitrile, epoxides.[7] The hydroxyl groups from wood react with isocyanates by forming a nitrogen-containing ester. Clermont and Bender[8] exposed wood veneer, swollen in dimethylformamide, to vapors of phenyl isocyanate at 100-125 °C. The resulting wood was very stable dimensionally and showed increased mechanical strength with little change in color. Baird[9] investigated the reaction of dimethylformamide-soaked cross-sections of white pine and Englemann spruce with ethyl, allyl, butyl, *t*-butyl and phenyl isocyanates. The reaction of isocyanate with wood is presented in Fig. 1.

By replacing some of the hydroxyl groups on the cell wall polymers with a chemical reagent, the hygroscopicity of the lignocellulosic material is reduced.[10]

The objective of this study was to investigate the changes of structural and thermal properties in two wood species (spruce and eucalyptus) after chemical modification using toluene-2,4-diisocyanate (TDI). The treated wood of these species can be further combined with other resources, such as plastics, glass, metals and synthetics, in order to obtain different composite materials.

Wood–OH + **R–N=C=O** → **Wood–O–C(=O)–NH–R**
isocyanate

Figure 1: Reaction of isocyanate with wood

EXPERIMENTAL

Materials

Eucalyptus wood, *Eucalyptus globulus*, (E) and spruce wood, *Picea abies*,(S), supplied by Sodra Company, Sweden, were ground in a Retsch PM 200 planetary ball mill. Uniform wood fibers of 0.42 mm in length have been obtained through grinding and sieving. Then, the wood samples thus prepared were washed with distilled water for 1 h under constant stirring at 80 °C, and dried in an oven at 100 °C until constant weight was achieved. The wood samples were identified by labels S_1 and E_1, respectively. The chemical composition of spruce and eucalyptus wood is shown in Table 1.

Table 1
Average content of holocellulose and lignin in spruce and eucalyptus wood species[11-13]

Wood species	Extractives (%)	Holocellulose (%)	Lignin (%)
Spruce	2.8	74.46	25.20
Eucalyptus	1.06-2.98	70	26

All analytical grade reagents (glacial acetic acid, hydrogen peroxide, ethyl acetate) were supplied by Chemical Company, Iasi, and were used as received. Toluene-2,4-diisocyanate (TDI) with purity >98% was supplied by Fluka, Germany.

Wood maceration

Dried wood samples (S_1, E_1) were immersed in glacial acetic acid, 120 vol. hydrogen peroxide and water in a percent ratio of 50:38:12 for 12 h, under continuous stirring at 60 °C. Then, the wood samples were washed with water until a pH of nearly 7 was reached, and were dried in an oven at 60 °C for 24 h. The wood samples thus treated were labeled as S_2 and E_2, respectively. TGA analysis indicated a moisture percentage of 4.6% in the wood samples. FTIR spectroscopy was used to characterize the S_2 and E_2 samples.

Chemical treatment of wood with isocyanate

Wood samples S_2 and E_2 (50 g) were placed in a 250 mL three-neck round-bottom flask, equipped with a magnetic stirrer, thermometer, condenser, and were soaked with 30 mL of ethyl acetate at 75 °C for 30 min under continuous stirring. 47 ml of toluene-2,4-diisocyanate (TDI), was added into the flask and the reaction was continued for 60 min more at the same temperature under continuous stirring. After that, the treated wood samples (labeled as S_3 and E_3) were filtered and washed three times with ethyl acetate and dried at 100 °C until constant mass. Dried S_3 and E_3 wood samples were characterized by FTIR spectroscopy and TG-DTG-DSC analysis.

FTIR-ATR spectroscopy

FTIR-ATR spectra were recorded using a spectrophotometer Vertex 70 model (Bruker, Germany) in the range of 4000-400 cm^{-1} with a 4 cm^{-1} resolution and a scan rate of 32. The spectrophotometer is equipped with MIRacle^{TM} ATR accessory designed for single or multi-reflection attenuated total reflectance (ATR) and a diamond crystal plate (1.8 mm diameter), allowing solid materials to be put in intimate physical contact with the sampling area through high-pressure clamping and yielding high-quality, reproducible spectra.

Water absorption

Wood samples (1.0 g) were used to determine the degree of water absorption. The samples were first placed in an oven set at 60 °C, under reduced pressure, for 8 h. The oven-dried weight (W_D) was determined and used to calculate the water absorption as follows:

$$WA (\%) = [(W-W_D) / W_D] \times 100$$

where W is the weight of the sample after water uptake in deionized water, at 20 ºC, for an absorption time of 28 h and 85% RH.

Thermal analysis

TG/DTG/DSC analysis was performed using a Netzsch STA 449 F1 Jupiter system under nitrogen atmosphere. The measurements were performed while heating the samples (~5 mg) placed in Al_2O_3 crucibles hermetically closed with lids, at a rate of 10 °C/min, from room temperature up to 600 °C, and using nitrogen as a purging gas at a flow rate of 50 mL/min. TG curves were analyzed using a Netzsch Proteus analysis software.

RESULTS AND DISCUSSION

Wood treatment with TDI

Wood is a composite material with different functional groups, which can produce a complex, cross-linked network with the isocyanates, due to its comparatively high functionality. The chemical treatment of S and E wood samples with peroxide in acidic medium determines the exposure of the hydroxyl groups to serve as binding sites for the reaction with TDI. This treatment extracts wood surface substances, such as fats, waxes and part of the hemicellulose and lignin.[14,15]

FTIR-ATR spectroscopy

FTIR spectroscopy was used to study chemical changes on the wood surface before and after chemical treatment. Untreated wood samples (S, E), those treated with water (S_1, E_1), further macerated wood samples (S_2, E_2), and TDI treated wood samples (S_3, E_3) have been characterized through FTIR-ATR analysis (Fig. 2).

Usually the broad peak around 3420 cm^{-1} is associated with mixed hydroxyl groups originating mainly from cellulose and hemicelluloses. The peak around 1058 cm^{-1} is a characteristic peak associated with C-O stretching mainly in cellulose and hemicelluloses from wood samples. The peak around 1630 cm^{-1} signals the characteristic absorption of conjugated carbonyl group C=O of lignin in wood samples.

The peaks around 1608 cm^{-1} and 1506 cm^{-1} represent the stretching of an aromatic ring framework in the lignin of wood.[16] The significant FTIR peaks and the corresponding groups and vibration type are listed in Table 2.

The formation of a urethane bond between wood hydroxyl groups and phenyl isocyanate was evidenced by strong absorptions at 1731 cm^{-1} (for S_3 and E_3) and 1244 cm^{-1}, characteristic of the C=O and C–N bonds, respectively, appearing after the chemical treatment with TDI. Additionally, strong absorption bands appeared at 1600 cm^{-1} and 1456 cm^{-1}, characteristic of the aromatic vibrations of the phenyl groups. The untreated and chemically treated wood behaved quite similarly at this point.

The relative values of the crystallinity index (χ_{IR}) and optical density(RVOD) were calculated from FTIR spectra (Table 3).[21]

The two wood species under study have different behavior due to the chemical treatment, a fact evidenced by the absorbance ratios and the relative values of optical density, presented in Table 3. The increase in crystallinity index and of the A_{OH}/A_{CH2} ratio indicates that the treated wood samples have an ordered structure, especially the spruce sample. The low relative value of optical density (for sample S_3) indicates that some lignin fragments were removed from wood during chemical treatment.

Table 2
Wavenumber values for main FTIR peaks, their corresponding functional groups and their vibration type for wood[17-20]

Wavenumber (cm^{-1})	Functional group	Vibration
2902-2910	$-CH_2-$	C-H stretching
1735-1741	R(C=O)OH	C=O stretching
1630-1649	C=O (conjugated)	C=O stretching conjugated with benzene ring
1506	aromatic ring	stretching of aromatic ring framework
1056-1060	C-O(H)	C-O stretching

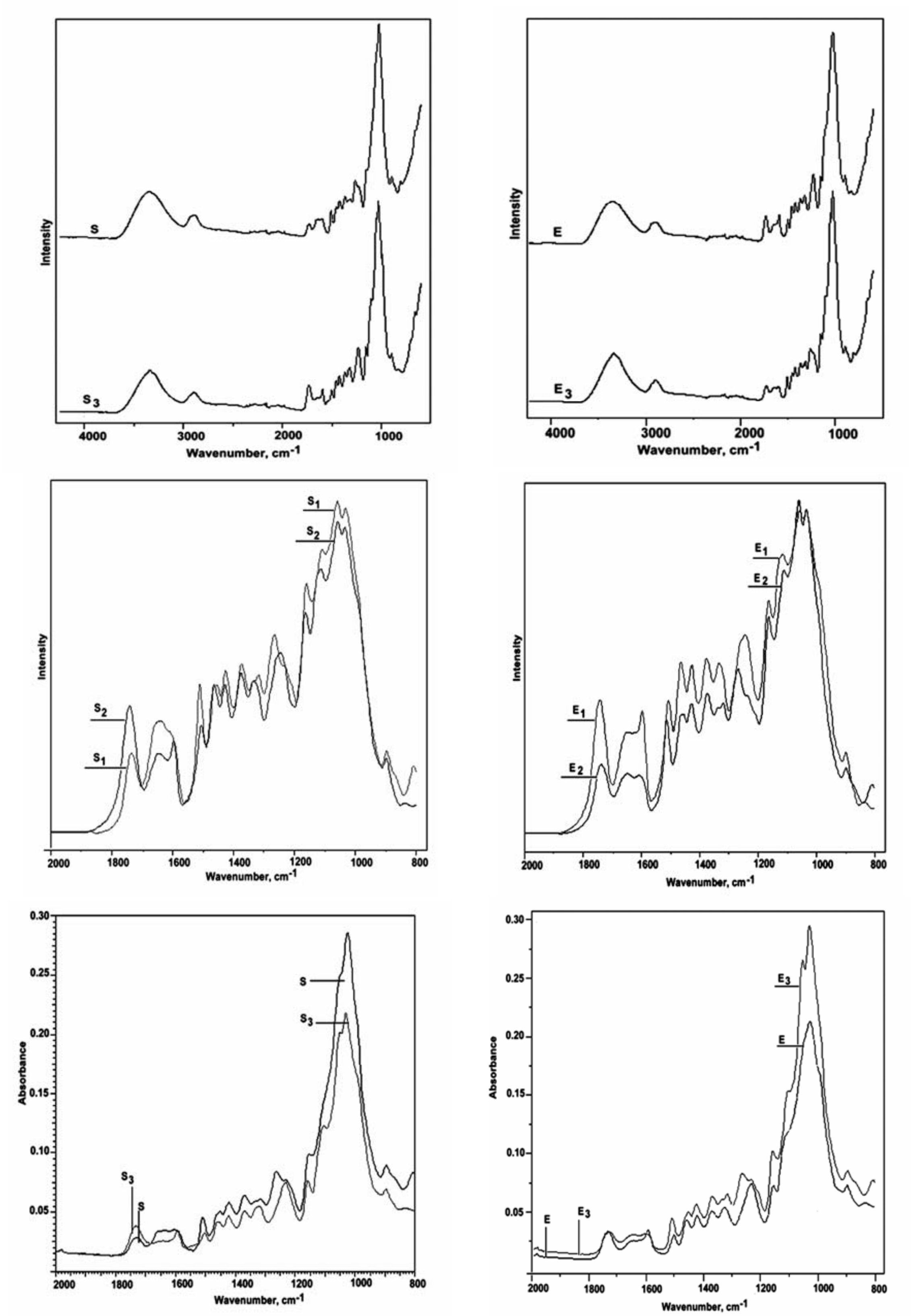

Figure 2: FTIR-ATR spectra of eucalyptus and spruce wood samples: untreated (S, E), treated with water (S_1, E_1), treated with water and macerated (S_2, E_2), and further treated with TDI (S_3, E_3)

Table 3
Different parameters of wood samples
before and after chemical treatment

Sample	χ_{IR} (%)		A_{OH}/A_{CH2} ratio		RVOD
	A_{1370}/A_{2900}	A_{1420}/A_{900}	A_{1315}/A_{1370}	A_{1315}/A_{2900}	A_{1505}/A_{1425}
E	1.761	0.649	1.055	1.857	0.652
E_3	1.547	0.671	1.035	1.602	0.791
S	1.617	0.639	0.939	1.519	0.778
S_3	1.650	0.663	1.085	1.791	0.672

Water absorption

The water resistance that wood presented after chemical modification is significant for new applications that are moisture-sensitive, such as exposure to environmental factors.

For both wood species, chemical modification determined a reduced water uptake (Fig. 4). The water uptake–time curves exhibit two well-separated regions. At short times, below 21 h, the kinetics of absorption is very fast, whereas at long times, over 21 h, the kinetics of absorption is slow and leads to a plateau, corresponding to an equilibrium of water uptake.

Thermal analysis

The thermal analysis of wood is difficult due to the composite nature of wood, which is constituted by a mixture of hemicelluloses, cellulose and lignin. Gronli and co-workers[22] studied the thermal degradation profiles of various hardwoods and softwoods in nitrogen atmosphere.

TG/DTG/DSC curves for spruce and eucalyptus wood samples (untreated and treated with TDI) are presented in Figs. 5 and 6. The time derivative of the mass fraction (DTG) curves of both spruce and eucalyptus wood samples were qualitatively similar to each other. Both of them showed two main regions of weight loss for hemicelluloses and cellulose degradation, respectively. Since lignin degrades over a wide range of temperature, it did not show a characteristic peak.

The initial weight loss observed between 20 °C and 120 °C is attributed to the vaporization of the water from the fibers, whilst the onset degradation of the wood fibers occurs at a higher temperature, precisely over 280 °C for spruce wood and 260 °C for eucalyptus wood. Above these temperature values, the thermal stability is decreasing. The first stage is associated to the thermal depolymerisation of hemicelluloses, pectin and the cleavage of glycosidic linkages of cellulose whilst, the second one corresponds to the degradation of cellulose present in the wood fibers. The decomposition of lignin occurs slowly within the whole temperature range. These results are also confirmed by the DTG curves.

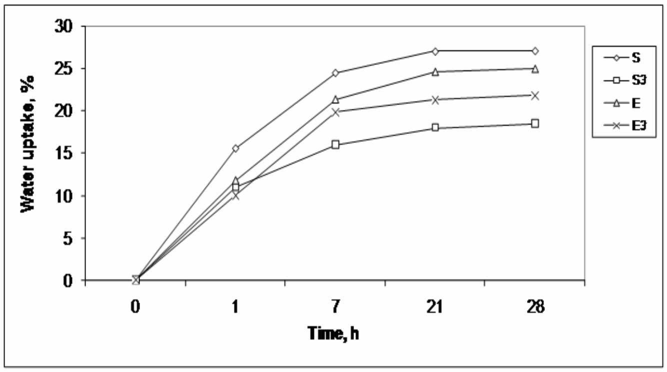

Figure 4: Water absorption results for untreated (S, E) and treated (S_3, E_3) wood samples

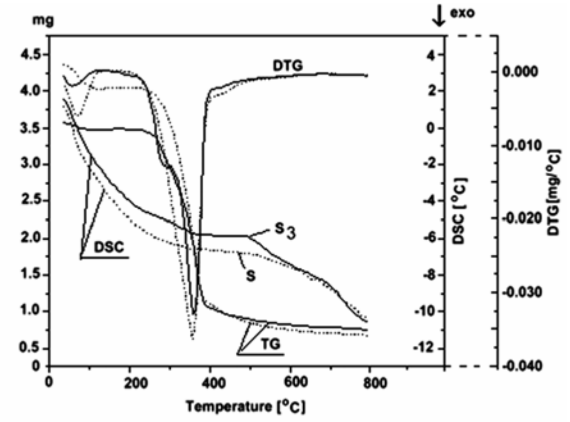

Figure 5: TG/DTG/DSC curves for spruce wood (S) and spruce wood treated with TDI (S_3)

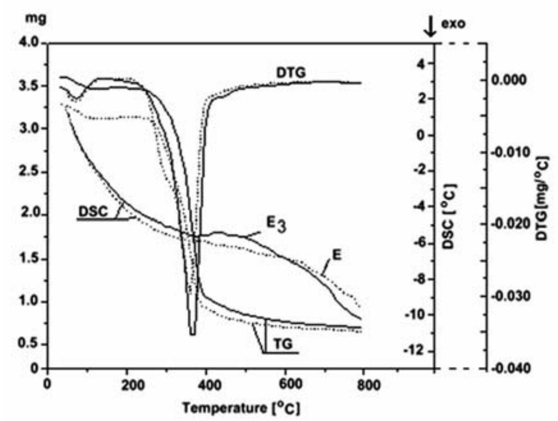

Figure 6: TG/DTG/DSC curves for eucalyptus wood (E) and eucalyptus wood treated with TDI (E_3)

Table 4
Temperature interval (T_i, T_m, T_f) and weight loss (Wt, %) of thermal decomposition of wood samples

Sample	T_i (°C)	T_m (°C)	T_f (°C)	Wt (%)	T_i (°C)	T_m (°C)	T_f (°C)	Wt (%)
S	52.2	72.2	95.7	6.87	282.7	359.6	487.6	72.5
S_3	44.4	62.5	89.5	2.27	257.4	362.4	377.8	77.5
E	49.8	69.9	99.3	7.74	261.8	356.6	370.4	74.3
E_3	60.4	66.2	92.5	3.06	290.6	364.5	451.4	77.6

The weight loss in the first region (20-120 °C) was small (6.8-7.7% for untreated wood and 2-3% for TDI treated wood). The weight loss in the second region (350-480 °C) was 73% for untreated wood and 77% for TDI treated wood. The temperature interval (T_i, T_m, T_f) and weight loss (Wt, %) of thermal decomposition of untreated and TDI treated wood samples are presented in Table 4.

The onset degradation temperature (T_i) of untreated wood is different from that of TDI treated wood. The TG thermal derivate (DTG) curves show that a wide peak appears around 100 °C, which can be associated with the maximum water loss rate. The untreated and TDI treated wood samples show a main one-stage degradation within the range of 250-480 °C, when the carbohydrates from wood were decomposed (Figs. 5, 6). Due to the rapid decomposition of cellulose, it showed a narrow peak followed by a rapid decay and a long tail. In the main domain of degradation, the maximum temperature (T_m) is higher for TDI treated wood (Table 4).

The study of the cure kinetics of isocyanate resins treated wood can been performed through dynamic scanning calorimetry (DSC).[23] The temperature range 210-360 °C mainly corresponds to cellulose and to some lignin fragments for the higher temperature range. The chemical modification of fibers changes the thermal response of the new materials, especially in the lignin range (temperature above 360 °C).

CONCLUSIONS

The behavior of spruce and eucalyptus wood species treated with toluene-2,4-diisocyanate was investigated. FTIR spectroscopy analysis evidenced the treatment of softwood and hardwood samples with toluene-2,4-diisocyanate. Due to the higher quantity of free hydroxyl groups present in the polysaccharides components of wood, the chemical reaction may have been mainly located on the holocellulose wood component.

The degradation of hemicelluloses during the treatment significantly reduces the amount of free reactive hydroxyl groups, thus decreasing wood reactivity. The changes in reactivity can have important consequences on wood transformation processes. For both wood species, the thermal stability of the isocyanate treated wood was lower than that of the untreated wood.

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