

Liquefaction of Wood, Synthesis and Characterization of Liquefied Wood Polyester Derivatives

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ABSTRACT: Liquefaction of Central-European softwoods meal was performed using a mixture of diethylene glycol and glycerol and a minor addition of *p*-toluenesulfonic acid as a catalyst. The liquefied wood was used as a replacement of a certain amount of the polyhydroxy alcohol in the polyester synthesis, enabled by the large number of hydroxyl groups that were available in the liquefied wood. Three different polyesters were synthesized by using adipic acid and phthalic acid anhydride as reagents. The products were characterized using FTIR, GPC/SEC,

and viscosity measurements. The polyesters have hydroxyl values that were reduced due to esterification, from 1043 mg KOH/g of the liquefied wood to 400–800 mg KOH/g. Polyhydroxyl alcohols (22–23%) in the polyester formulations were replaced by wood derivatives. Such saturated polyesters are suitable for further use in polyurethane foam production. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1265–1271, 2010

Key words: wood liquefaction; polyester; characterization

INTRODUCTION

Biomass based materials and wood in particular are among the more abundant renewable resources. Much effort has been devoted to converting these types of biomass into useful industrial and commercially viable products. Recently, considerable attention has been given to the preparation of environmentally friendly, polymeric products from liquefied biomass materials. However, much remains to be done in synthesis, analysis and characterisation if these new materials are to be exploited to their full advantage. With respect to the liquefaction of wood and wood wastes, earlier applications were mainly based on their use as fuels.¹ A direct liquefaction of wood at high temperatures and pressures, to convert it into a more usable fuel, was achieved using different technologies,² thus providing a longer term solution to the need to decrease the crude oil dependency.^{3,4}

The liquefaction of wood, via derivatisation, can be achieved using phenol, sulphuric acid being present as the catalyst.^{5–7} These products have similar properties to those of conventional phenolic resins and have been used as adhesives and as starting materials in molding compounds.

The liquefaction/derivatisation mechanism is not fully understood. Several attempts to elucidate the mechanisms associated with the liquefaction of lignin, of cellobiose and of cellulose have been published. The liquefaction of lignin with phenol has been studied on the basis of the behavior of model substances, such as guaiacylglycerol- β -guaiacyl ether. According to Lin et al., the dominant products were guaiacylglycerol- α -phenyl- β -guaiacyl ethers, followed by guaiacol, triphenylethanes, diphenylmethanes, benzocyclobutanes and phenylcoumaranes.^{8,9}

The behavior of cellulose in acidic ethylene glycol was studied by Yamada and Ono.¹⁰ These authors proved the formation of ethylene glycol-glucosides in the early stage of liquefaction. These later decomposed into the 2-hydroxyethyl levulinate. Jasiukaityte et al.¹¹ studied the liquefaction of different types of cellulose by monitoring the molar mass decrease and changes in degree of crystallinity during the reaction. They found that the less disordered regions degraded in the initial minute of liquefaction. The highly ordered cellulose regions remained relatively stable for a longer time. Kobayashi et al.¹² have undertaken research into the liquefaction of cellulose powder, of steamed lignin and of mixtures of these two components to characterize the reaction process on the basis of the polyhydric alcohol nature of the materials. They found that condensation reaction occurred only in mixtures of cellulose and lignin. Under these conditions, dimethyl formamide insoluble residue was formed, being similar in

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nature to wood. They suggested that a condensation reaction occurred between the depolymerised cellulose residues and the aromatic derivatives of lignin. Budja et al. utilized this self condensation reaction for crosslinked polymer film formation¹³ The efficiency of liquefaction and the time needed for the complete liquefaction was reduced significantly, using microwave radiation as the heating source.^{14,15} Complete liquefaction was achieved in 20 min under the prevailing processing conditions.

Zavrel et al. very efficiently dissolved wood chips in ionic liquids, an environment-friendly alternative to conventional methods¹⁶

Liquefied wood (LW) can be considered to be a polyhydric alcohol. In the liquefaction process, the hydroxyl group-containing species in the wood components can be used as polyols for several different purposes. The polyhydric units that are present in the resulting liquefied/derivatised wood can be used in the creation of polyurethane foams, polyurethane resin precursors¹⁷ and in the recently developed wood-polyalcohol based urethane adhesives.¹⁸ Several authors have found a combination of PEG-400 and glycerol to be the most effective liquefying reagent.¹⁹⁻²¹ Claims are made that greater than 95% liquefaction has been achieved in most experiments. These final products have similarities with the liquid wood that was used directly without any additional treatment. It is claimed that mixtures of such liquefied/derivatised mixtures can be directly used for the preparation of polyurethane foams.²² The products are rich in ethylene oxide units and, due to the presence of extensive hydrogen bonding, they have highly hydrophilic character. Lee et al.²³ have studied the thermal stability, biodegradability and genotoxicity of a range of polyurethane foams that were produced from polyols made from waste paper. They found that the foams possessed the same thermal stability as those made from liquefied starch or wood. The foams were biodegradable to some extent. No mutagens or carcinogenic substances were found in water extracts from the foams. These materials are technologically simple and inexpensive to produce. It is stated that they can be used in agricultural and horticultural applications.

The hydroxyl value of the liquefied wood has been determined by several authors and is generally determined to be between the equivalent of 200 and 500 mg KOH/g. The actual value depends on the liquefaction time. This large number of hydroxyl group sites means that the products have applications in those areas in which the hydroxyl component can be used in complex polyester synthesis. Yu et al.²⁴ liquefied corn stover in a mixture of ethylene glycol and ethylene carbonate and used the liquefied product as a polyol in a condensation reaction with different organic dibasic acids. The

product was a completely crosslinked solid polyester, insoluble in most solvents.

Saturated polyesters are defined as polyesters whose components contain no polymerizable double bonds, the opposite of what occurs with alkyd resins and unsaturated polyesters.²⁵ Saturated polyesters are synthesized by the condensation of bifunctional or polyfunctional monomers containing hydroxyl or carboxylic groups. The hydroxyl groups in the current investigation originate from liquefied wood. The polycondensation process takes place at temperatures of 150–260°C. Water as the main reaction byproduct, is removed from the system by the creation of a slight vacuum, gas stream condensation or an azeotropic process. The polycondensation reaction can be accelerated by adding an esterification catalyst such as lithium hydroxide, di-*n*-butyl tin oxide or other compounds. This type of polycondensation usually yields linear polyesters with a molecular mass up to 7000 g/mol or branched polyesters with a molecular mass of up to 5000 g/mol.

Some benefits could be expected from such systems. These include the incorporation of the biomass components into the polymeric compositions and consequently, the provision of a certain degree of biodegradability. Esterification of a proportion of the hydroxyl groups reduces the reactivity of the LW, a feature that is sometimes desired in polyurethane synthesis. The work presented here offers a new approach to the utilization of liquefied/derivatised wood in the creation of novel polymeric composite materials.

EXPERIMENTAL

Materials

Wood meal of spruce (*Picea* spp.) was sieved through a 2 mm screen and dried at room temperature to a constant water content (10% w/w).

Glycerol, diethylene glycol, adipic acid (ADA), phthalic acid anhydride (APA) and di-*n*-butyl tin oxide were of reagent grade and were used without further purification.

METHODS

Liquefaction of wood meal

The respective polyhydroxy alcohol mixture of glycerol (240 g) and diethylene glycol (60 g), *p*-toluenesulphonic acid (9 g) were placed into the 1000 cm³, three necked glass reactor, equipped with mechanical stirring. The mixture was heated with constant stirring to 160°C. Then the wood (100 g) was added gradually and the temperature raised to 180°C. The liquefaction reaction was carried out for 120 min. A sample was withdrawn periodically from the

reaction system and immersed in cold water to quench the reaction. The extent of liquefaction was evaluated by determining the residue after the dilution of the sample with dioxane and water (4 : 1 v/v). The diluted sample was then filtered using Whatman fast flow filter paper. The residue on the filter paper was dried in an oven at 120°C, to constant weight. The residue ratio was calculated as the weight percentage based on the starting wood material.

Synthesis of polyester polyols from the LW

Three different formulations with two different dibasic organic acids were used to study the differences in the physical and the chemical properties of the final products. Three hundred gram of liquefied wood were used in combination with 60 g of ADA, the resulting polyester was identified as P1. With 60 g of phthalic acid anhydride, the product was identified as P2. With 30 g of ADA and 30 g of phthalic acid anhydride, the resulting polyester was identified as P3.

The liquefied wood was introduced into the four-necked 1000 cm³ glass reactor, equipped with a water condenser and mechanical stirrer. The reactor was placed in an electric jacket heater. ADA and/or phthalic acid anhydride were added when the liquefied wood reached 180°C. Dibutyl tin oxide (0.2% w/w) was added as the esterification/transesterification catalyst. The mixture was heated gradually up to 200°C, under stirring and was held at this temperature. Water was continuously distilled from the reaction system. A slight stream of nitrogen was introduced into the reactor for easier transport of water vapor into a condenser. A sample was withdrawn periodically from the reaction system and its acid value was determined. The total reaction time was between 160 min and 180 min. After completion of the reaction, when the acid value was reduced to less than 30 mg KOH/g, the reaction mixture was cooled to ambient temperature.

Scanning electron microscopy (SEM) observations

Wood meal and wood residue, after the liquefaction reaction, were micrographed on a FE-SEM SUPRA 35 VP, Carl Zeiss scanning electron microscope. Samples were sputter coated with a thin layer of gold to avoid electrostatic charging during scanning.

Viscosity measurements

The viscosity of polyesters and of the liquefied wood was measured using a VISCO STAR PLUS rotational viscometer. Samples were diluted with

dioxane to 50% (w/w) before measurement and thermostated to 25°C. Spindle R-6 was used at 200 rpm. Liquefied wood was assessed in its undiluted state.

Measurement of hydroxyl number and acid number of LW and of liquefied wood polyester derivatives

The hydroxyl numbers²⁶ (ASTM Standard D4274-05) of LW and its derivatives were determined as follows: 0.5 g to 1.0 g of sample was dissolved in 25 cm³ of a phthalation reagent and heated at 115°C for 1 h under reflux. This was followed by the addition of 50 cm³ of pyridine through the condenser. The mixture was back-titrated with a 0.5 M sodium hydroxide solution. The indicator was a 1% phenolphthalein solution in pyridine. The phthalation reagent consisted of 115 g of phthalic anhydride, dissolved in 700 cm³ of pyridine.

The hydroxyl number, defined as mg KOH/g of sample was calculated as follows:

$$\text{Hydroxyl number} = \frac{(B - A) \times M \times 56.1}{w} + \text{acid number}$$

Here, A is the volume of the 0.5 M sodium hydroxide solution required for the titration of sample (cm³), B is the volume of the sodium hydroxide solution required for the titration of the blank solution (cm³), M is the molarity of the sodium hydroxide solution and w is the amount of the sample (g).

If the sample is acidic, the acid uses the phthalation reagent during the analysis and the hydroxyl number must be corrected accordingly.

The acid number²⁷ was determined as follows: 0.4 g of sample was weighed into a 400 cm³ Erlenmeyer flask and dissolved in 50 cm³ of solvent mixture. The solvent mixture consisted of dioxane and water (4 : 1 v/v). 0.5 cm³ of phenolphthalein indicator solution (1% in ethanol) was added and titrated with 0.1 M KOH solution in ethanol to the equivalent point. The acid number (mg KOH/g of sample) was calculated using the following equation:

$$\text{Acid number} = \frac{(C - B) \times M \times 56.1}{w}$$

Here, C is the titration volume of the potassium hydroxide solution (cm³), B is the titration volume of blank solution (cm³), M is the molarity of the potassium hydroxide solution and w is the amount of the sample (g).

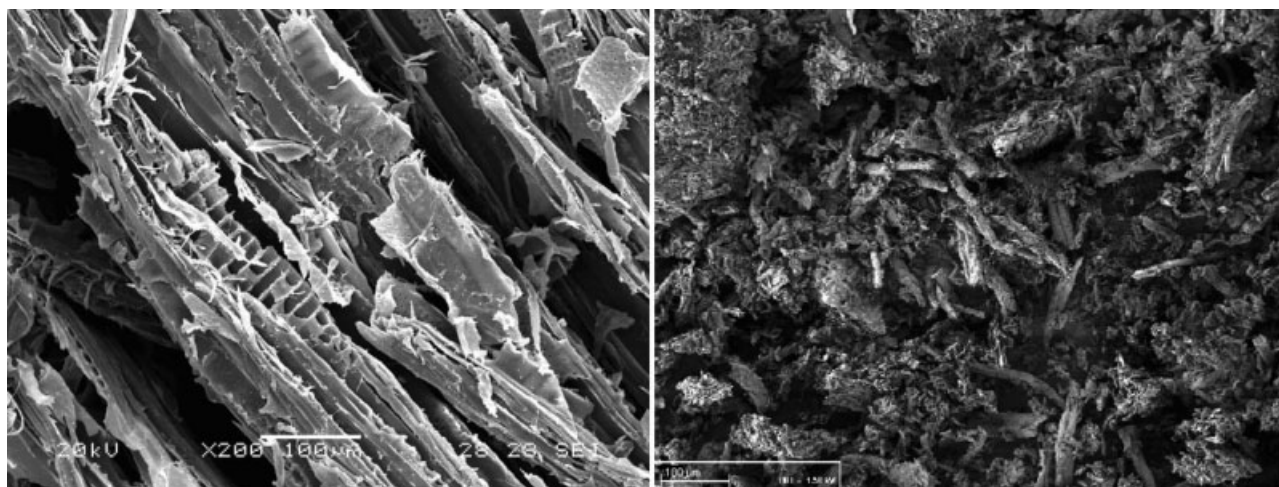


Figure 1 Wood meal (left) and the residue after the liquefaction process (right).

FTIR spectroscopic analysis

All of the spectra were obtained using a Perkin-Elmer Spectrum-1 FTIR spectrophotometer. The liquid/derivatised wood samples and the polyesters were each supplied on a NaCl crystal as a thin film. Transmittance spectra were measured in the wavelength range from 4000 cm^{-1} to 500 cm^{-1} .

GPC measurements

Gel permeation chromatographic representations were obtained on an HP – AGILENT system, consisting of isocratic pump HP 1100, a refractive index detector AGILENT 1100 and a Perkin-Elmer LC235 diode array detector. A PLgel column MIXED-D, $5\text{ }\mu\text{m}$ was used. Polystyrene standards were used for the calibration curve. The mobile phase was prepared from dimethyl acetamide containing 0.05 M LiBr. The latter was added to prevent interaction between the sample molecules and the stationary phase.

RESULTS AND DISCUSSION

Wood meal of spruce was liquefied and used as the feedstock for the synthesis of three different polyester polyols. Polyester polyols were prepared by using adipic acid and/or phthalic acid anhydride in a high temperature polycondensation/esterification reaction. The yield of the liquefaction process was determined and polyester polyols were characterized using FTIR, GPC/SEC and viscosity measurements.

Measurement of residue content

The liquefaction process gave yields of liquefied wood in excess of 99%. However, in all cases, a

small amount of residue was present in the liquefied wood solution. The residue of between 0.22 and 0.25% of the original mass of the liquefied wood was achieved because of the selected, short reaction time during which the condensation between the cellulose oligomers and lignin had not yet started.¹⁰

SEM analysis of residues from the wood meal liquefaction process

The wood particles that remained after the liquefaction process were analyzed by SEM. Figure 1 shows an SEM micrograph of the wood meal sample. The left hand representation illustrates the original wood meal. The right hand side image represents the small amount of residue that was left after the liquefaction procedure.

Because of the liquefaction procedure, the wood cells become completely disintegrated. The residue appears to contain only irregular, powdery particles of wood fragments, perhaps mixed with some of the products of the polycondensation process that occur towards the end of the liquefaction processes.

Characterisation and analysis of the liquefied wood and its polyester products

The liquefied wood and its polyester products were characterized using FTIR spectroscopic evaluation, gel permeation chromatography/size exclusion chromatography (GPC/SEC) and viscosity measurements.

FTIR spectroscopic evaluations

The FTIR spectra of the polyesters that were synthesized from the liquefied wood meal with adipic, phthalic acid anhydride and their combination are shown in Figure 2. The FTIR spectrum of the

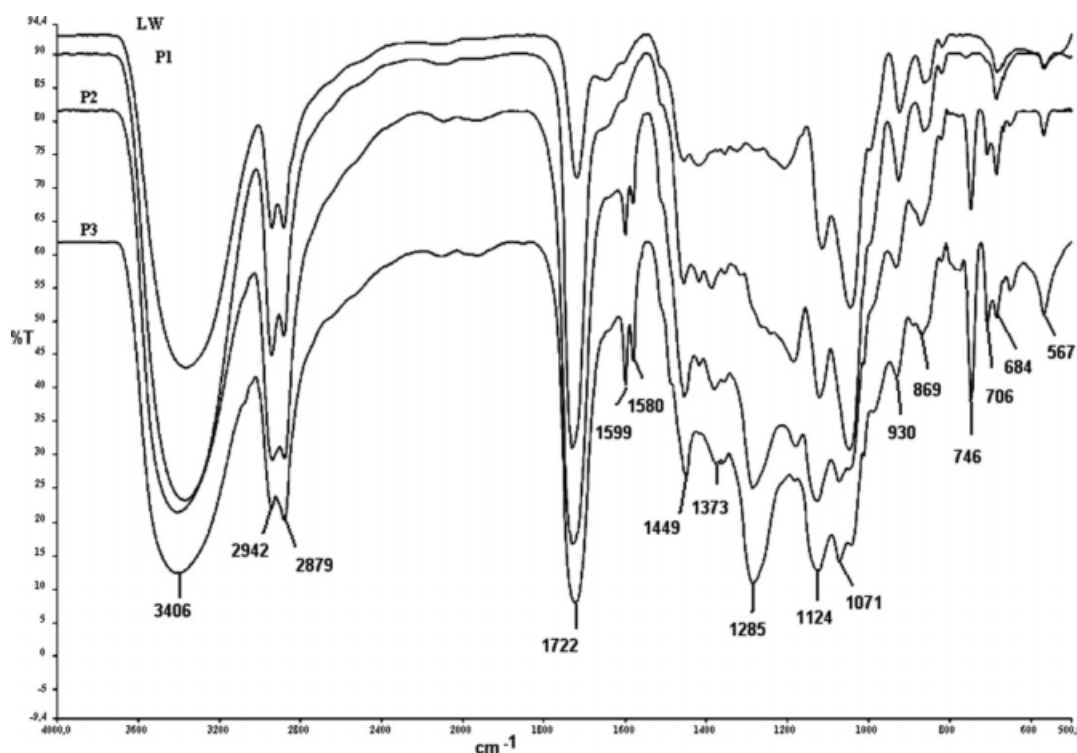


Figure 2 FTIR spectrum of the LW, adipic acid polyester (P1), phthalic acid anhydride polyester (P2) and a mixed adipic and phthalic acid anhydride polyester (P3).

liquefied wood as the starting material is also shown in Figure 2.

The following interpretation is offered. The intense broad band between 3370 cm^{-1} and 3410 cm^{-1} indicates the presence of OH groups in large quantities in LW as well as in the polyester products. In the polyesters, the band intensity is reduced to a certain extent due to partial esterification process.

The intense band at 1722 cm^{-1} indicates the presence of the carbonyl group of the ester function, such as the ADA ester denoted in the spectrum as P1, the phthalic acid ester in the spectrum denoted as P2 and a mixture of both in the spectrum denoted as P3.

The bands at 1599 cm^{-1} and 1580 cm^{-1} indicate the aromatic skeletal vibrations of the phthalic acid based components in P2 and P3. The weak absorbance at 1373 cm^{-1} provides evidence of the aromatic products after the breakdown of the lignin macromolecules. The bands between 1071 cm^{-1} and 1285 cm^{-1} are mainly due to C—O—C and the C—OH arrangements, arising from ethereal and alcoholic units respectively. Those, between 930 cm^{-1} and 684 cm^{-1} respectively, indicate the presence of the aromatic double bonding. Those at 746 cm^{-1} and 706 cm^{-1} respectively are due the presence of O-substituted benzene ring. These bands in the liquefied wood spectrum indicate the presence of the aromatic lignin based components.

GPC/SEC analysis of liquefied wood meal based materials

The liquefied wood meal (LW) and the corresponding polyester based materials, that were derived from reaction between the liquefied wood meal and adipic and/or phthalic acid anhydride were subjected to GPC/SEC analysis. All of the molar masses are expressed as average molar masses, calculated from the calibration curve based on polystyrene standards. Figure 3 gives the chromatograms

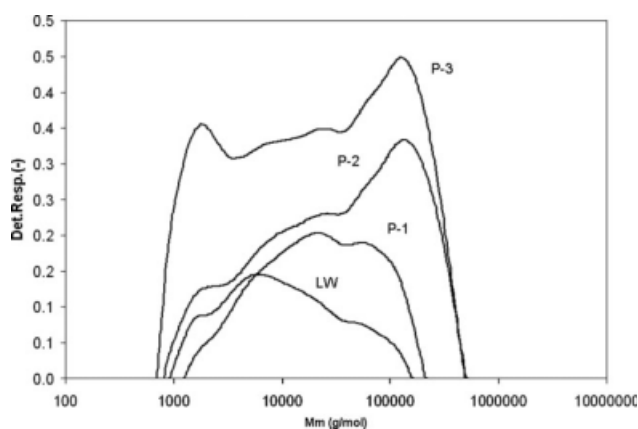


Figure 3 GPC/SEC chromatograms of the liquefied wood (LW) and corresponding polyester derivatives: adipic acid polyester (P-1), phthalic acid anhydride polyester (P-2) and a mixed adipic and phthalic acid anhydride polyester (P-3).

TABLE I
Characteristic Data of Polyesters and the Initial Liquefied Wood

	M_n (Av.) g/mol	M_w (Av.) g/mol	PDI	OH value mg KOH/g	Viscosity Pa s	% of wood (w/w)
LW	4790	19400	4.0	1043	0.7	24
P-1	10300	39900	3.9	798	1.9	22
P-2	4590	60000	13.1	378	1.9	23
P-3	7980	79500	10.0	437	2.2	23

derived from the liquefied wood meal and polyesters.

LW denotes the molar mass distribution of the liquefied wood with the maximum at 5600 g/mol. Considering that the molar masses of the cellulose macromolecule are in the range of the 1000,000 g/mol, the reduction in polymer chain length and corresponding molar mass is evident. The further esterification with ADA gave the polyester (P-1) with a four times higher molar mass than that of the LW, with the maximum at 22,000 g/mol.

The esterification with phthalic anhydride (P-2) gave even higher molar masses, with the maximum at 110,000 g/mol, indicating the greater reactivity and greater efficiency of the phthalic anhydride in the esterification reaction. The chromatogram denoted as P-3 gives three peaks, one at a lower average molar mass, at 1700 g/mol originating from low molar mass fragments from the liquefaction reaction, the second peak at 25,000 g/mol which is in the range of the ADA polyester and the highest peak at 120,000 g/mol, which is in the range of the pure phthalic acid anhydride polyester. Such a multimodal distribution of the molar masses is shown also in the polydispersity index, which is higher for the pure phthalic polyester and for the mixed acids polyester. A certain proportion of low molar mass derivatives is observed in all of the polyester chromatograms, indicating that esterification took place only partially, as proven by the partial reduction of hydroxyl values. This way, a rise in the average molar mass was achieved, together with a reduction in the hydroxyl group content. Such a modification of the polyester reactivity and complexity is a favorable factor with respect to subsequent use of these materials in polyurethane synthesis. Rigid polyurethane foams, for example, are produced using polyester polyols with hydroxyl values in a range of about 350 to 500 and highly hydrophobic, rigid polyurethane foams from polyester polyols with average molar mass up to 10,000 g/mol.²⁸

Wood content in final products and hydroxyl values

In Table I, characteristic data of three different polyesters and of the initial liquefied wood are

summarized, such as average molar mass values, OH values, viscosity values and the wood content.

The OH value per unit mass of dry wood cannot be calculated precisely. However, there have been studies of wood that has been exposed to deuterated or tritiated water, where the number of accessible OH groups was estimated. A theoretical OH content, based upon the composition given by Fengel and Wegener²⁹ (1989) has also been made, giving a total OH content of 1110 mg KOH/g of dry wood. Since OH groups are involved in hydrogen bonding between the cellulose chains within the crystalline core of the microfibrils, they are considered to be inaccessible. Therefore, the number of accessible OH groups is not known precisely. However, in using the above mentioned methods the authors have estimated the OH content between 447 mg KOH/g to 386 mg KOH/g, depending on the origin of the wood species and the water content.

Theoretically all of the hydroxyl groups could be esterified during the polyester synthesis. A liquefied wood, with a hydroxyl value of 1000 mg of KOH/g for complete esterification, would need 17.8 mM/g of organic acid. However, such a complete reaction is never achieved due to differences in reactivity of the hydroxyl groups. A certain proportion of the hydroxyl groups is left unreacted since, in the case of the polyurethane synthesis, the hydroxyl groups are needed for the polycondensation reaction with the polydiisocyanate.

In the current study, the hydroxyl value has been reduced from 1043 mg KOH/g to values between 400 and 800 mg KOH/g. Since the amount of residual glycol in the sample was determined by gas chromatographic analysis, it was possible to calculate the theoretical OH value for the glycols that were present in the reaction mixture. The OH value of products, originating from the wood meal, was then calculated as the difference between the OH value of the sample and the OH value of the glycols, respectively. It was possible to distinguish between the contribution of the remaining glycols to the total OH value and to the liquefaction products of wood components, ranging from 400 mg KOH/g to 200 mg KOH/g. These OH groups, including those of the remaining unreacted glycols were available for the esterification reactions.

As a result of the utilization of liquefied wood in polyester-polyol synthesis, 22–23% of the polyhydric alcohols were replaced with wood. The reactivity and the hydroxyl value remained in the range required for commercial products.

CONCLUSIONS

Liquefied wood was used as a component in polyester synthesis due to the large number of hydroxyl groups that are available in the liquefied wood. The liquefied wood was used as a substitute for part of the polyhydroxy alcohols that are standard raw material in polyester formulation. Three different polyesters were prepared using adipic acid and/or phthalic acid anhydride. The polyesters were prepared under the standard high temperature polycondensation conditions, confirming the use of the liquefied wood as a raw material in polyester synthesis. The products were characterized using FTIR, GPC/SEC and viscosity measurements showing similar properties to those possessed by equivalent commercial polyesters such as Desmphen[®] S saturated polyesters from Bayer Material Science, Pittsburgh. A rise of the average molar mass was achieved together with a reduction of the hydroxyl group content. Such a modification of the polyester reactivity and complexity is favorable for further utilization in polyurethane synthesis. The final OH values of the polyesters were in the range of saturated polyesters that are used in polyurethane production. The use of wood in these experiments replaced up to 23% of polyhydroxy alcohols in polyester formulations. This amount varies according to product requirements and can be increased significantly.

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