

FRACTIONATION OF CIMV WHEAT STRAW LIGNIN AS AN APPROACH FOR PROMOTING ITS INTERACTION WITH ISOCYANATES AND CHARACTERISTIC OF PRODUCTS OBTAINED

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High degree of lignin OH-groups conversion in the reaction with isocyanates is an important factor to obtain lignopolyurethanes with high physical-mechanical performance. In comparison with commercial polyols CIMV organosolv lignin has some inferior properties: low solubility in solvents usually used for chemical reaction with isocyanates and occurrence of non-uniformity of OH-groups, which contribute to different nucleophilicity and steric hindrance. To increase the reactivity of lignin, fractionation of CIMV lignin was performed by extraction with different organic solvents. This was studied by reaction of lignin and its fractions with isocyanates. Besides CIMV lignin, five its fractions were obtained and investigated: 2 fractions obtained by separate extractions with dioxane and methanol and 3 fractions obtained in the process of sequential extraction of CIMV lignin with dichloromethane, methanol and methanol/dichloromethane mixture. The functional groups and component composition of fractions were characterized by wet chemistry methods, NMR, FTIR spectroscopy and Py-GC/MS. Interaction of lignin samples with 4,4'-diphenylmethane diisocyanate (MDI) was investigated in extra dry dioxane (DOX) in argon atmosphere at 25°C. The initial concentrations of OH groups (lignin) and NCO groups (MDI) were 0,3 mol/l for all experiments. Concentration of catalyst used (dibutyltin dilaurate) was 0,0075 mol/l. FTIR spectroscopy (absorbance band at 2273 cm⁻¹) was used for monitoring the NCO group disappearance during reaction. The second order rate constants were calculated for lignin and its fractions up to 40-50% of NCO conversion. CIMV lignin was characterized by a weak reactivity in reaction with MDI due to its low solubility in DOX. The maximum NCO conversion did not exceed 35%. In contrast, all lignin fractions were fully solubilized in DOX and complete NCO conversion was accompanied resulting in gel-like lignopolyurethanes. Reactivity of fractions was not equal. The highest rate constant ($4,7 - 4,9 \cdot 10^{-4} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) was detected for both methanol soluble lignin fractions. Non-fractionated CIMV lignin is capable to interact with polymeric MDI in heterogeneous conditions without any solvent (confirmed using differential scanning calorimetry (the reaction enthalpy 19 kJ/mol). The results obtained show the prospects of CIMV lignin as macromolecular polyol for polyurethane synthesis and as reactive component/filler in polyurethane composites.

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