

The wheat straw lignin as a renewable polyol of polyurethanes elastomers.

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Elaboration of sustainable processes with the most profitable utilization of all products obtained in the technological cycle is the basic position of modern biorefinery concept. Lignins separated as by-products in the result of lignocellulosics chemical processing can be considered as a renewable aromatic polyols suitable for crosslinked polyurethane (PU) production. Structural heterogeneity, the weak solubility of parent technical lignins in organic solvents and low reactivity with isocyanates restricts its application as macromonomer in PU systems. The sequential solvent fractionation of technical lignin enhancing the lignin uniformity, solubility and reactivity with isocyanates was realized in the present work.

The novel wheat straw organosolv lignin (BIOLIGNINTM) produced on CIMV pilot plant (France) was sequentially extracted with organic solvents of different polarity (dichloromethane, methanol and dichloromethane/methanol mixture). The fractions obtained were characterized in terms of its structure, functionality and composition using FTIR spectroscopy, PY-GC/MS and methods of wet chemistry. Interaction of lignin samples with 4,4'-diphenylmethane diisocyanate (MDI) was investigated in extra dry dioxane (DOX) in argon atmosphere at 25°C in the presence of dibutyltin dilaurate as catalyst. FTIR spectroscopy (absorbance band at 2273 cm⁻¹) was used for monitoring the NCO groups disappearance during reaction. Parent lignin was characterized by a weak activity 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 achieved resulting in gel-like lignopolyurethanes formation. The second order rate constants were calculated up to 40-50% of NCO conversion. The highest rate constant ($4.7 \times 10^{-4} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) was determined for methanol soluble fractions because of highest content of aliphatic OH groups.

In this study the effects of lignin on the properties of PU elastomers obtained from three components systems including polyethylene glycol (Mn=400 g/mol) as a soft segment, fractionated lignins and commercial polymeric diphenylmethane diisocyanate Voratec SD 100 were investigated. PU elastomers were prepared by pre-polymerization of constituents in extra dry tetrahydrofuran followed by solution casting on PTFE bottom for curing. The content of lignin fractions in PU varied in the range 5-40%. The cross-link density of the PU was determined experimentally by Flory-Rehner method using dimethylformamide as a swelling agent. The increase of cross-link density of PU from $0.25 \times 10^{-3} \text{ mol/cm}^3$ for PEG-MDI system up to $1.0-1.5 \times 10^{-3} \text{ mol/cm}^3$ for lignin containing PU films was established. As the results the tensile elastic modulus (E), tensile strength (σ) and glass transition temperature of LPU films were increased steadily with growth of lignin content in PU compositions. The most pronounced increment was determined for PU containing methanol/ dichloromethane soluble lignin fraction coinciding with its highest functionality. The data of thermal analysis of PU in oxidizing media have shown the antioxidative impact of lignin fractions at their low ($\leq 5\%$) content

in PU. At more significant content in PU fractionated wheat straw lignin acts as a promoter of charcoal formation at a high temperature impact on polyurethanes.

Acknowledgment:

The financial support from 7th Collaborative project BIOCORE contract 241566 is gratefully acknowledged.