

Study of the reactivity of Kraft and organosolv lignins with 4, 4'-diphenylmethane diisocyanate and characterization of the obtained products

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Abstract

The interaction of two types of lignins: Kraft lignin (KL), isolated according to the LignoBoost process (Sweden), and Alcell organosolv (OL) lignin (Canada), with 4,4'-diphenylmethane diisocyanate (MDI) in the dry dioxane media at 298 K was investigated. In the presence of dibutyltin dilaurate (DBTD) reaction followed the second order rate up to 43-56 % conversion. In these conditions the second order rate constants for both lignins are approximately $3.7-3.8 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$. After that the negative deviation from the second order kinetic was observed. The complete NCO conversion in the case of KL takes more time than that of OL.

The data of FTIR spectroscopy, element analysis and results of thermal analysis indicate the complete condensation of OH groups of both lignins with MDI, followed by crosslinked polyurethane (PU) formation.

Introduction

The modern "biorefinery" conception is aimed to the elaboration of sustainable processes with maximal profitable utilization of all products obtained in technological cycle. Lignins separated as by-products in the result of lignocellulosic chemical processing are recognized as an important renewable macro monomers. Owing to the presence of hydroxyl groups lignin can be considered as natural polyol suitable for PU production. PU are considered as one of the most versatile polymeric materials offering a wide range of products: foams, adhesives, coatings etc. A lot of scientific works aimed to lignin exploration in PU systems has been done in the world during the last few years. Structure, solubility, functionality of lignins varies depending on plant source and methods of their isolation. Correspondingly, different lignins display the different reactivity in reaction with isocyanate and properties of lignin derived polyurethanes will be varied in dependence of lignin type used. In the last years the new method of Kraft lignin removing from black liquor LignoBoost process was developed by Innventia AB. The comparison of reactivity toward MDI of new type of KL LignoBoost with that of well known Alcell OL is the aim of this study.

Experimental

The content of different origin OH groups in lignin was determined by acetylation procedure followed by potentiometric titration and by acid-base conductometric titration [1].

The chemical interaction of KL and OL lignins with MDI was realized in the extra dry dioxane (DOX) solution in argon atmosphere at 298K in glass reactor equipped with the thermostatic jacket. The initial concentration of OH groups (lignin) and NCO groups (MDI) was 0.3 mol/l for all experiments. Concentration of DBTD used was 0.0075 mol/l. FTIR spectroscopy Perkin-Elmer Spectrum One equipped with Horizontal Attenuated Total Reflectance Sampling Accessory was applied for monitoring the NCO group (absorbance at 2273 cm^{-1}) disappearance during the reaction. Four repeated experiments have been done for each type of lignin.

After achievement of ~95% of NCO conversion the products of condensation was removed from reactor and solvent was distilled. The solids were heated during 8 hours at 80°C and then were extracted with dichloromethane. The insoluble and soluble fractions were characterized by FTIR spectroscopy (4000-600 cm⁻¹). C, H, N content in fractions determined using Analysis System Vario MACRO CHNS. Differential scanning calorimetric (DSC) analysis was provided with a device METLER TOLEDO DSC 823 in the temperature range from -50°C till 200°C at heating rate 10°C/min.

Results and discussion

In comparison with Alcell lignin (OL) LignoBoost Kraft lignin (KL) is characterized by the higher content of OH groups (mainly aliphatic) able to condensation with isocyanates (Table1).

Table 1. The functional composition of KL and OL lignins

Sample	Number of OH groups per C9			
	OH _{ph.}	OH _{aliph.}	OH _{COOH}	OH _{total}
LignoBoost KL	0,40	0,88	0,18	1,46
Alcell OL	0,40	0,57	0,14	1,11

Such functional composition of KL promotes formation of the net of intra and inters molecular hydrogen bonds of enhanced density that leads to growth of glass transition temperature (T_g) up to 158 °C in comparison with 87 °C for OL.

The second order rate constants for OL and KL lignins in the beginning stage of the reaction with MDI were practically the same: $3.8 \pm 0.4 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$ and $3.7 \pm 0.3 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$.

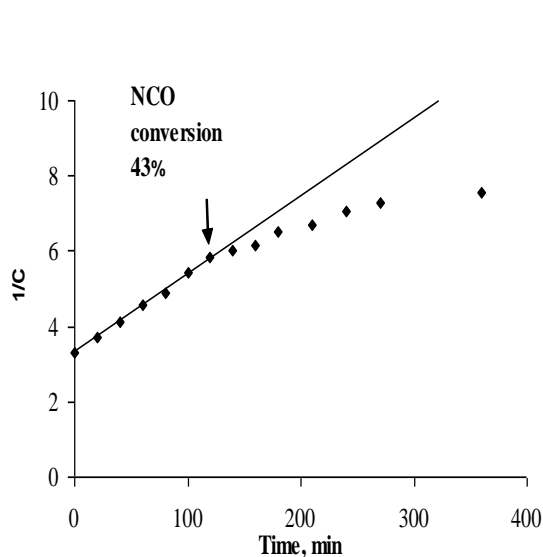


Figure 1. The second order plot of KL reaction with MDI in DOX/DBTD solution at 298K

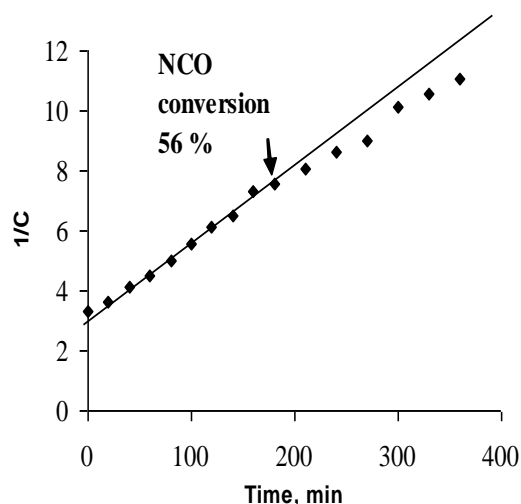


Figure 2. The second order plot of OL reaction with MDI in DOX/DBTD solution at 298K

It was shown that for both lignin in the presence of catalyst the reaction corresponds to second order equation up to definite NCO conversion value when homogeneous reaction conditions are observed. (Figure 1-2). For KL this NCO conversion value were lower than that for OL lignin and the negative deviation from the second order started earlier that can be explained by earlier formation of crosslinked PU structures because higher functionality of KL. The results obtained are in good conformity with theory of gel (cross-linked network) formation during the reaction of diisocyanates with polyols of different functionality [3]. As the result the complete conversion of NCO in KL-MDI system takes more time in spite of the second order rate constants for OL and KL lignins in the beginning stage of the reaction with MDI were close.

According FTIR data the methylene chloride dissolved fraction (yield ~5%) included mainly DBTD with a small amount of the aromatic component. The complete condensation of both lignins with MDI accompanied by the high yield of lignopolyurethanes cross-linked fraction was proved by FTIR spectroscopy, elemental analysis and DSC method.

Conclusions

Cross-linked ligno-polyurethanes with the lignin content more then 50% were obtained. The close reactivity of both LignoBoost lignin and Alcell lignin with MDI before ~45% of NCO conversion was observed. The complete NCO conversion in the case of KL takes more time than that of OL.

The presented results allow considering LignoBoost lignin as well as Alcell lignin as a prospective renewable aromatic polyols, which can be used as a cross-linked agent for the regulation of rigidity and thermostability of PU foams, adhesives and coatings.

References

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