

Polyoxometallate catalyzed oxidative modification of lignin as a favorable pre-treatment for copolymerization with propylene oxide for polyurethanes production

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In the present work lignin, extracted from wheat straw in organic acid media (product of a novel biomass refinery technology developed at CIMV, France), was subjected to oxidative modification. The regimes of oxidative modification catalyzed by $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ (POM) increasing content of lignin hydroxyl groups, in particular carboxyl groups (more than twice) and not accompanied by degradation of the lignin polymeric structure have been developed earlier (EcoBalt 2012). Such oxidizing of lignin before its oxypropylation can be considered as a favorable pretreatment stage of lignin because increasing the amount of reactive sites able to copolymerization with propylene oxide.

The modification was performed using as reoxidant for POM (1) oxygen of air or (2) H_2O_2 under moderate conditions: pressure of 1 bar and temperatures of 90°C (O_2 reoxidant) and 50°C (H_2O_2 reoxidant). The effect of the oxidative treatment on the lignin functionality and structure was evaluated using Py-GC/MS, solid state ^{13}C NMR and chemical analysis.

It was established that use of the H_2O_2 reoxidant in the process of lignin oxidation was more promising in comparison with the O_2 , because it allowed to increase the content of targeted hydroxyl groups, at significantly lower demand of POM (approximately by 25 times) and temperature of the process (50°C against 90°C).

The oxypropylation of the parent and oxidized lignins with propylene oxide (PO) was studied in high pressure Parr reactor using KOH as a catalyst. It was shown that oxypropylation of lignin pre-oxidized in the system POM/ H_2O_2 proceeded in the similar manner as the parent lignin but the rate of the process was some lower due to the presence of higher amount of $-\text{COOH}$ groups with lower nucleofility. Oxypropylation of lignin oxidized in the system POM/ O_2 proceeded dramatically slower and was characterized by high residual pressure of non-reacted PO, and high amount of solids fraction (~30%) in reaction products. This can be explained by the neutralization of alkali catalyst by $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ presented in the lignin oxidized by POM/ O_2 as an admixture. Therefore, the method of lignin pre-oxidation in the system POM/ H_2O_2 was chosen in order to obtain polyols for polyurethanes (PU) production.

The composition of polyols obtained from the parent and oxidized lignins, their functional characteristics and reactivity with isocyanate were studied. Both the parent lignin and oxidized lignin based polyols were applied in composition of cross linked PU elastomers. The tensile and thermal properties of PU obtained were measured and compared.

The results obtained have shown that the oxidative modification by POM/ H_2O_2 can be considered as an approach to lignins upgrading for production of high reactive lignopolyols suitable in the field of polyurethane chemistry.

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