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Preparation of rigid polyurethane foam from lignopolyol obtained through mild oxypropylation

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Lignin, one of the main components of lignocellulose, can be used as an alternative to chemical polyols in the production of polyurethane because of its abundant phenolic and alcohol hydroxyls. Traditionally, lignin is directly applied in the preparation of polyurethane; however, modified lignin has been proved to be superior, especially that obtained by the oxypropylation reaction. Therefore, lignopolyol obtained by mild and efficient oxypropylation was utilized in the production of rigid polyurethane foam in this study. Specifically, the effects of the content of lignopolyol on the chemical structure, morphological structure, mechanical properties and thermal stability of the lignin-based rigid polyurethane foam were investigated. It was found that the compressive strength of the rigid polyurethane foam was significantly improved with the addition of lignopolyol compared with that of the pure polyurethane foam, which was attributed to the fact that oxypropylation made lignin into highly branched and functionalized polyols by transforming all phenolic hydroxyls into aliphatic hydroxyls. Moreover, when the molal weight of lignopolyol accounted for 40% of the added polyols, the generated foam showed optimal uniformity and regularity, and the compressive strength reached 0.18 MPa, meeting the requirements of industrial application, below which, the amount of undesired reactions is bound to increase. As a consequence, the added amount of lignopolyol was increased as much as possible on the basis of guaranteeing the desired properties, which was more conducive to realizing the green degradation and economic synthesis of rigid polyurethane foam.

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Introduction

In 1937, polyurethane was synthesized for the first time by Otto Bayer, and has rapidly developed into a diversified and widely used plastic industrial product with a growing global market share, which can be applied in various fields including transportation, construction, furniture, food processing, textiles and garments, and health care.¹ Polyurethane foam is the polyurethane material with the largest market demand, accounting for more than 50% of polyurethane products, the main characteristics of which are its porosity, low density, and high specific strength.² According to the different kinds of raw materials and the change in formula, soft, semi-rigid and rigid

polyurethane foams with different densities and performance can be produced and used for different purposes.³

Of these, rigid polyurethane foam is a kind of highly cross-linked polymer with a compact cellular structure and low thermal conductivity,⁴ which has been widely used as an insulating and structural material in the fields of insulation, construction, transportation and decoration, and takes up almost one third of the polyurethane market.⁵ Rigid polyurethane foam is generally prepared by the reaction of a polyether (polyester) polyol and polyisocyanate in the presence of a foaming agent, catalyst, foam stabilizer and other additives. Annually, approximately 1.3 billion pounds of polyols are used in North America to produce rigid polyurethane foam, accounting for 50% of the polyol market.⁶ However, these polyols are mainly derived from petrochemical intermediates on an industrial scale. Therefore, in order to achieve the sustainability of the environment and economy, seeking renewable resources to partially or completely replace petrochemical polyols has become a key issue in the sustainable development of polyurethane materials.⁷ Lignin, one of the main components of lignocellulose, has abundant phenolic and alcohol hydroxyls,⁸ which can be used as an alternative to polyols.⁹ Approximately 50 million tons of industrial lignin as a major by-product are produced in the pulp and paper industry every year, yet the

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majority is not utilized and only burned as fuel, resulting in a great waste of resources and potential environmental pollution.^{10,11} As a consequence, utilizing lignin instead of chemical polyols to produce polyurethane materials is a beneficial method for environmental protection, resource utilization and economic cost.

At present, lignin-based polyurethane foams are mainly synthesized in two ways: (1) directly using lignin to react with isocyanate and (2) through chemically modifying lignin to prepare polyurethane.¹² Due to its high molecular weight, low solubility in polyols and small number of aliphatic hydroxyl groups of lignin, crude lignin, directly incorporated into polyurethane foam instead of petroleum-based polyols, exhibits a low replacement ratio.⁵ In contrast, the chemical modification of lignin is more conducive to achieving a high amount of addition and can further improve the properties of polyurethane foam.¹³ There are various methods to modify lignin, including hydroxylation, oxypropylation, liquidation, and amination, the properties of which differ for each type of chemical modification.¹⁴ Of these, oxypropylated lignin has been extensively studied and proved to be superior in the production of polyurethane.^{15,16} It had been found that under alkaline conditions, oxypropylated lignin with more secondary alcohol hydroxyl groups can be generated, while in the liquefaction reaction, more primary alcohol hydroxyls are generated.¹⁷ Additionally, Ahvazi *et al.* pointed out that the secondary alcohol hydroxyl was more liable to react with isocyanate to produce polyurethane.¹⁸ Hence, lignin modified by oxypropylation under alkaline conditions is more suitable for the preparation of polyurethane.

Typically, the oxypropylation reaction of lignin is performed under certain relatively strict and tedious conditions;¹⁹ however, a mild, efficient and simple method for the preparation of lignopolyol has been reported in our previous work,²⁰ which has not been studied in the production of polyurethane. Therefore, in this study, the effect of lignopolyol obtained by the above-

mentioned oxypropylation on the properties of rigid polyurethane foam has been investigated, particularly the amount of lignopolyol added in, which could achieve cost savings and environmental protection on the basis of ensuring performance.

Results and discussion

In the preparation of lignin-based rigid polyurethane foam, the hydroxyl value and molecular weight of the selected lignin are important parameters for replacing industrial polyether polyols. The specific properties of the lignopolyol used in this study are as follows: the weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (M_w/M_n) were 2714 g mol⁻¹, 1526 g mol⁻¹ and 1.78, respectively. The content of primary hydroxyls was 1.50 mmol g⁻¹ and that of secondary hydroxyls was 2.71 mmol g⁻¹, while phenolic hydroxyls were not present, as previously reported.²⁰ Subsequently, the effects of the content of lignopolyol on the chemical structure, morphological structure, mechanical property and thermal stability of the lignin-based rigid polyurethane foam were mainly investigated. The foam samples were labelled LPF₁, LPF₂ and LPF₃ according to the added ratios of lignopolyol and polyether polyol (PEG-400) of 2 : 8, 3 : 7 and 4 : 6, respectively, and the control sample without lignopolyol was named PF₀.

Chemical structures of the rigid polyurethane foam

The chemical structure of the rigid polyurethane foam was identified by FT-IR, as presented in Fig. 1. The absorption peak near 2300 cm⁻¹ was attributed to the unreacted -NCO, which might be derived from the excess PMDI.²¹ Comparing the spectra, it was observed that the unreacted -NCO increased with the increasing proportion of added lignopolyol, which was probably because the increased lignopolyol could influence its

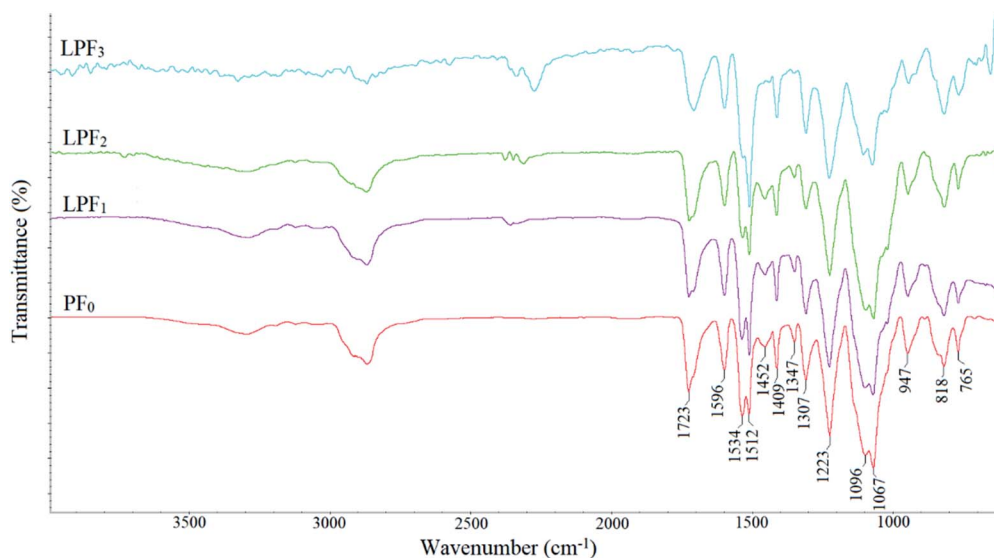


Fig. 1 FT-IR spectra of the rigid polyurethane foams.



dispersion in the foam, thus affecting the reactivity of lignopolyol. The absorption at 1723 cm^{-1} , corresponding to the characteristic vibration peak of the -CO= group, represents the basic carbon structure of polyurethane rigid foam.²² The bands at 1596 cm^{-1} , ascribed to the absorption vibration of CO-NH , and 1534 cm^{-1} , assigned to the bending vibration of N-H , are characteristic absorption peaks of polyurethane monomers.²³ In addition, the signals at 1409 and 1096 cm^{-1} (C-N coupled, C-O stretch) also indicated the presence of polyurethane linkages, confirming the chemical coupling between the active hydroxyl groups (polyether polyol and lignopolyol) and isocyanates.²⁴ Moreover, the N-H deformation of isocyanurate was identified at 1512 cm^{-1} , which was on account of the side reaction between the isocyanate and urethane groups.²⁵ The peaks of the conjugated and non-conjugated C-O stretching at 1223 and 1067 cm^{-1} , respectively, and aromatic C-H deformation at $800\text{--}600\text{ cm}^{-1}$ were also detected. An obvious phenomenon was also observed wherein, with the increase of lignopolyol, especially when the ratio of lignopolyol and polyether polyol was $4 : 6$, the absorption peak at 1534 cm^{-1} weakened and that at 1512 cm^{-1} significantly enhanced, indicating that the amount of undesired reactions began to increase.

Morphological structures of the rigid polyurethane foam

In order to understand the cellular morphology inside the foam, SEM was performed to analyze the rigid polyurethane foams. As shown in Fig. 2, the cell shape of the pure polyurethane foam without lignopolyol (PF_0) was uneven and irregular, and part of the cell structure was distorted or broken, which might be due to the fact that the relatively small molecular weight of PEG-400 did not provide enough support in the synthetic foam. With the incorporation of lignopolyols, the cellular shape became much

more regular, while still being not uniform, which can probably be attributed to the lignopolyol affecting the process of cell nucleation in the preparation of polyurethane foam. Additionally, it was observed that with the increase in the proportion of lignopolyol, LPF_1 showed large differences in cell size, and the small cells accounted for a large proportion, while the difference in the cell size of LPF_2 became smaller, and the cells were relatively larger. The increased cell size indicated that fewer cells formed within a given volume, leading to decreased foam density, which was consistent with the subsequent apparent density. Moreover, the cells of LPF_3 (with the ratio of lignopolyol to polyether polyol of $4 : 6$) exhibited the highest uniformity and regularity.

Apparent density and compressive strength of the rigid polyurethane foam

The apparent density and compressive strength of all the foam samples are shown in Fig. 3. The density of the pure polyurethane rigid foam PF_0 was 0.096 g cm^{-3} , while after the addition of lignopolyol, the density of LPF_1 first increased to 0.120 g cm^{-3} . With the further increase in lignopolyol, the density of LPF_2 sharply decreased to 0.044 g cm^{-3} , and that of LPF_3 slightly rose to 0.053 g cm^{-3} . The change in apparent density was closely related to the morphological structure of the lignin-based polyurethane rigid foam, which was completely consistent with the phenomenon observed by SEM. Specifically, LPF_1 had more small cells, so the density was the largest per unit volume, in contrast to the larger cell sizes of LPF_2 , which led to fewer cells and the lowest density. Therefore, the appropriate addition of lignopolyol would reduce the density of the foams, which is actually desirable if the foam is to be used as packing or insulation material.

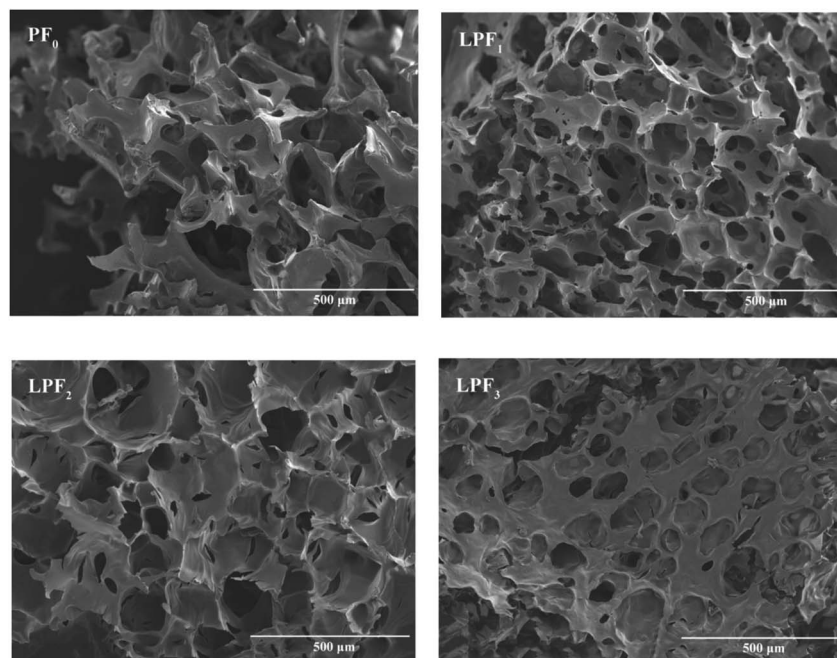


Fig. 2 SEM images of the rigid polyurethane foams.



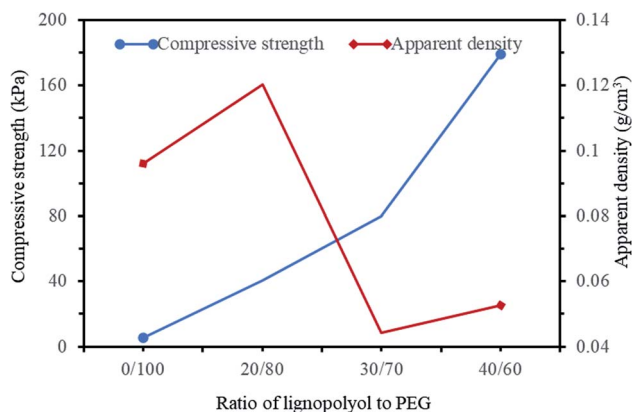


Fig. 3 The apparent density and compressive strength of the rigid polyurethane foams (ratio of ligninopolyol to PEG: molar ratio of the hydroxyl groups from ligninopolyol to those from PEG).

As can be seen from Fig. 3, the compressive strength of rigid polyurethane foam significantly increased with the addition of ligninopolyol compared with that of the pure polyurethane foam, which was ascribed to the fact that all the phenolic hydroxyls were transformed into aliphatic hydroxyls in the oxypropylated ligninopolyol, as reported in our previous study,²⁰ converting lignin into highly branched and highly functionalized polyols, as depicted in Fig. 4.²⁵ Therefore, the strength of the foam after

the reaction of ligninopolyol with isocyanate was obviously higher than that of PEG-400. Furthermore, as shown in the SEM image (Fig. 2), the internal pores of the pure polyurethane foam were distorted, and became uniform after adding ligninopolyols, which is another reason for the increase in strength, because a complete cell structure suggests high compressive strength.²⁶ Meanwhile, with further addition of ligninopolyol, the compressive strength increased, indicating that more aliphatic hydroxyls (especially secondary alcohol hydroxyls) reacted with isocyanate, leading to better mechanical properties of the polyurethane rigid foam, although there was still unreacted $-NCO$ remaining, as depicted in the above-mentioned FT-IR spectra (Fig. 1). When the ratio of ligninopolyol and polyether polyol reached 4 : 6, the compressive strength reached 0.18 MPa, demonstrating that it had reached the application requirements of many industrial polyurethane rigid foam materials, and could be used in building insulation material.²⁷

Thermal properties of the rigid polyurethane foam

The effect of ligninopolyol on the thermal properties of the rigid polyurethane foam materials was investigated by thermogravimetric analysis, and the corresponding TGA and DTG curves are shown in Fig. 5. The mass loss below 150 °C was caused by the evaporation of water. The pyrolysis of the lignin-based rigid polyurethane foam began at about 200 °C, indicating the breakage of polyurethane polymer chains, and the main

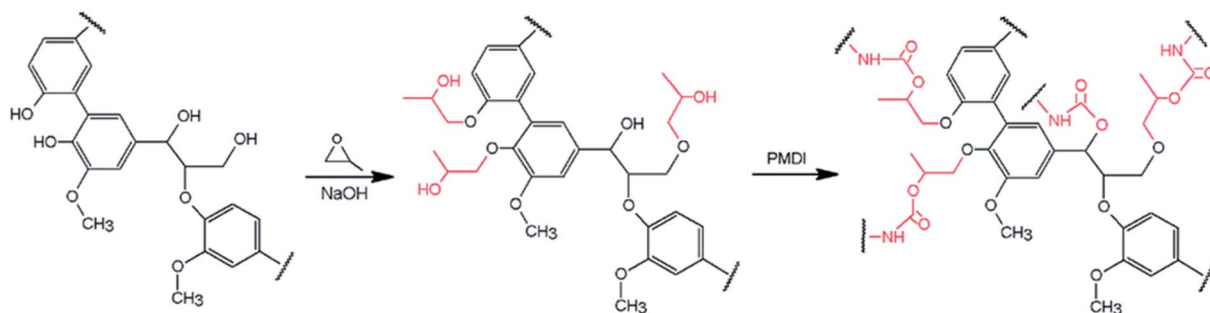


Fig. 4 Schematic of the reaction mechanism of lignin-based rigid polyurethane foam.

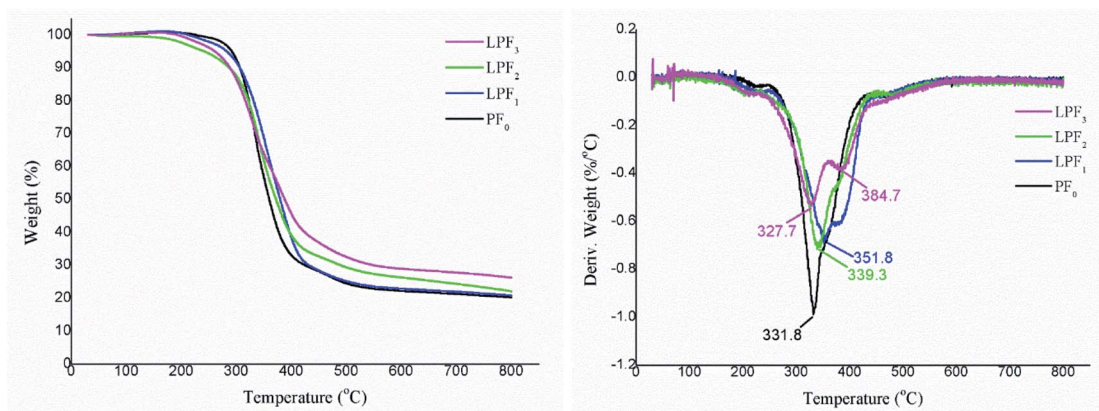


Fig. 5 TGA and DTG curves of the rigid polyurethane foams.



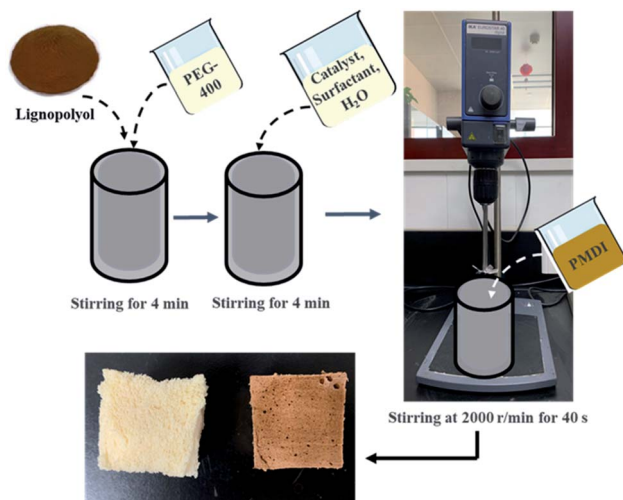


Fig. 6 The flow diagram of the preparation of lignin-based rigid polyurethane foam.

decomposition occurred between 250 °C and 450 °C.²² The maximum mass loss rate was around 350 °C, which produced diisocyanates and polyols along with other decomposition products such as amines, olefins and carbon dioxide.^{21,25} The final carbon decomposition of LPF₁ and PF₀ occurred similarly at 800 °C, and that of the remaining samples followed the order of LPF₃ > LPF₂ > LPF₁, demonstrating that the lignin-based polyurethane had higher thermal stability than pure polyurethane, and the carbon decomposition was related to the content of lignin in polyurethane.²³ In addition, the DTG curve shows that the maximum degradation temperatures of the lignin-based polyurethane foams (LPF₁–LPF₃) were slightly higher than that of pure polyurethane (PF₀), while the maximum mass loss rates (DTG-max) of the former were significantly lower than the control foam, which was ascribed to the higher density of aromatics in the lignin-based polyurethane foam network.²⁸

Conclusions

In this study, lignopolyol obtained through a mild and efficient oxypropylation modification was applied in the production of rigid polyurethane foam. The effects of the added amount of lignopolyol on the chemical structure, morphological structure, mechanical properties and thermal stability of lignin-based rigid polyurethane foam were investigated. The results show that in comparison with the pure polyurethane foam, the compressive strength of rigid polyurethane foam was significantly improved with the addition of lignopolyol. Meanwhile, the produced foam with the ratio of added lignopolyol and polyether polyol of 4 : 6 showed the highest uniformity and regularity, and its compressive strength reached 0.18 MPa, meeting the application requirements of certain industrial polyurethane materials. Therefore, the whole process, including the mild oxypropylation and addition of as much lignopolyol as possible, is beneficial to the further extensive application of industrial lignin in polyurethane materials.

Experimental

Materials

Lignopolyol was prepared by an efficient and mild integration process including the extraction and oxypropylation of lignin from agricultural waste corn stalk, as reported in our previous article.²⁰ Specifically, lignin was first obtained by hydrothermal pretreatment at 150 °C for 1 h, followed by alkaline treatment with 1 M NaOH at 70 °C for 2 h. Subsequently, the above extracted lignin fraction was modified by mild oxypropylation, that is, with the ratio of lignin to propylene oxide of 2 : 1 mg mL⁻¹, NaOH was added as a catalyst and the reaction was conducted at room temperature for 5 days. The obtained lignopolyol product was dried in an oven at 105 °C before being used to prepare polyurethane foam.

Polymeric methylene diphenyl diisocyanate (PMDI) with an isocyanate (–NCO) content of 7.45 mmol g⁻¹ was provided by DOW Chemicals. Polyethylene glycol (PEG-400, molecular weight 400 g mol⁻¹, hydroxyl content 5.75 mmol g⁻¹) as the polyether polyol and dibutyltin dilaurate (DBTL) as the catalyst were purchased from Aladdin Biochemical Technology Co., Ltd The surfactant AK-8805 was generously supplied by Maysta Chemical (Jiangsu, China). All other chemicals were purchased from Sigma-Aldrich Company (Beijing).

Production of the rigid polyurethane foam

The lignin-based rigid polyurethane foam was produced by a one-shot method, and the specific operation process was as follows (Fig. 6): the polyether polyol (PEG-400) and the prepared lignopolyol were mixed in a plastic beaker and stirred evenly for 4 min. Subsequently, 0.4 g of the catalyst (dibutyltin dilaurate), 0.4 g of the surfactant (AK-8805) and 0.8 g of the blowing agent (water) were added and thoroughly stirred for 4 min. A certain amount of PMDI was then added according to the NCO/OH ratio of 1.05, and the mixture was stirred vigorously at a speed of 2000 r/min for 40 s until bubbles formed. The obtained lignin-based rigid polyurethane foam was finally left in a fume hood for a week for curing before the sample was collected for analysis. The addition ratios of lignopolyol and polyether polyol (PEG-400) were 2 : 8, 3 : 7 and 4 : 6, which were the ratios of the hydroxyl values, and the total hydroxyl value remained constant. These samples were labelled LPF₁, LPF₂ and LPF₃, respectively. Additionally, the control sample without lignin, with only the addition of 10 g PEG-400, was prepared by the above method, and the product was named PF₀.

The addition amounts of lignopolyol, PEG-400 and PMDI were determined according to the molar ratio of –NCO and –OH. The specific formula used is as follows:

$$\text{NCO/OH} = M_{\text{MDI}} \times W_{\text{MDI}} / (M_{\text{L}} \times W_{\text{L}} + M_{\text{P}} \times W_{\text{P}}) \quad (1)$$

where W_{MDI} , W_{L} and W_{P} represent the masses (g) of PMDI, lignopolyol and PEG-400, respectively. M_{MDI} is the molar amount (mmol g⁻¹) of –NCO in PMDI, and M_{L} and M_{P} are the total hydroxyl molar contents (mmol g⁻¹) in lignopolyol and PEG-400, respectively.



Characterization of the rigid polyurethane foam

SEM images of the rigid polyurethane foams were captured on a Hitachi scanning electron microscope (S-3400 N, Tokyo, Japan) operating in the high-vacuum mode at an acceleration voltage of 5 kV. All the samples were first cut into small pieces with a wallpaper knife, and then coated with a thin layer of gold using a KYKY ion sputtering device (SBC-12, Beijing, China) prior to observation. The FT-IR spectra of the rigid polyurethane foams were recorded with a Bruker Tensor 27 FT-IR spectrometer (Bruker Corporation, Germany) equipped with ATR accessory in the range of 600–4000 cm^{-1} . The apparent densities of the foam samples were calculated using the weight and volume according to ASTM D1622-03. The mechanical properties of the foam samples were measured by a Zwick universal material testing machine (Z005, Germany). A specimen with a size of 20 mm \times 20 mm \times 15 mm was cut off each foam, and the compressive strengths at 20% deformation parallel to the foam rise direction were determined according to ASTM D1621. The thermal stability of each foam sample was tested with a simultaneous thermal analyzer (TGA/DSC1, Mettler Toledo, the United States), which was weighed in the range of 5–8 mg and then heated from 30 to 800 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C min}^{-1}$ under a nitrogen atmosphere with a flow rate of 20 mL min^{-1} .

Conflicts of interest

There are no conflicts of interest to declare.

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