

Lignin-Polyurethane Based Biodegradable Foam

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Abstract

Natural sources like starch and lignin used during manufacturing of polyurethane (PU) foam have been used extensively from last decades and replaced petro-chemical based PU foam due to their lower environmental impact, easy availability, low cost and biodegradability. Bio-renewable sources, such as lignin which is an abundant, underutilized component of cellulosic biomass, constitute a rich source of polyol which are being considered as polyol for the production of “eco-friendly and bio-degradable” PU foam. Lignin was mainly used for production of high fungal degradable polyurethane foams, followed by elastomers as well as wood adhesives. This review paper will focus on the progress of research in lignin based polyurethane materials for foam application.

Keywords

Lignin, Polyurethane, Foam, Biodegradable, Polyol

1. Introduction

1.1. Polyurethane Foams

With numerous advantages, such as light weight, good heat insulation, excellent strength and corrosion resistance, electrical insulating properties, sound absorbing properties and low density, the consumption of polyurethane foams (PUFs) has grown rapidly, and the PUFs become indispensable part in our daily life [1]. The foams have been developed into many types and classes of products, such as insulation materials for apartment houses, cold stores, pipelines. PUFs are prepared by the polymerization of isocyanates with polyols, in which the reacting mixtures are foamed using one or more blowing agents.

The foam formation process consists of various steps:

- Mixing of the monomers and bubble nucleation,

- Rise of the liquid foam,
- Phase separation, which leads to rapid modulus rise and cell opening, and formation of foamed elastomers [2] [3] [4].

1.2. Bio-Waste from Industry

Biomass obtained from industrial residues has considerable potential as a resource for industrial production [5] [6] [7]. Industrial residues ordinarily have homogeneous qualities and are cheap. Accordingly, products derived from residual materials are competitive in the market when characteristic properties of new products are similar or better than those derived from petroleum. Among numerous kinds of industrial residues, lignin is obtained on a large scale and is currently utilized only in a limited field [8]. Various types of industrial lignin are produced, not only as a byproduct of pulp and paper production [9] [10] [11] but also as bio-fuel production [12] [13].

2. Need of Lignin as Raw Material in Polyurethane Foams

Many kinds of rigid PU foams with different properties are widely used in construction industry, energy saving building and floating field. With the attention to the reduction of petroleum resources and the world environmental problems, however, the biodegradable polyurethane prepared by biomass, partially instead of polyol has aroused people's wide interests. Some researchers have studied how to synthesize PU foam by using modified starch and beeswax, but the price of these industrial raw materials is higher than that of the industrial lignin. The industrial lignin would have an obvious potential for using as the raw material of PU foam.

3. Advantages of Lignin

Lignin presents several advantages that make its utilization quite attractive in a wide range of applications.

Advantages:

- Readily available in huge quantities.
- If disposed as a waste, black liquor constitutes a serious environmental pollution hazard and therefore their valorization is of interest.
- High energy content due to its aromatic nuclei.
- Several reactive points available for chemical reactions [14].

4. Type of Lignins

Commercially available lignins are, most often, Kraft, soda and lignosulfonates associated to the corresponding most commonly used industrial processes for wood delignification and fibres isolation [15].

5. Lignin Chemical Structure

A renewable and promising source for sustainable chemicals and bio-based po-

lymeric materials is lignin with random cross-linking of the sub-structural phenyl propane units, and the physical and chemical properties are highly dependent on the isolation processes. The higher order structure of lignin is fundamentally amorphous with phenylpropanoid units such as shown in **Figure 1**, p-coumaryl alcohol, coniferyl alcohol and/or synapyl alcohol cross-linked to produce a three-dimensional lignin polymer via a radical coupling process during its biosynthesis as shown in **Figure 2**.

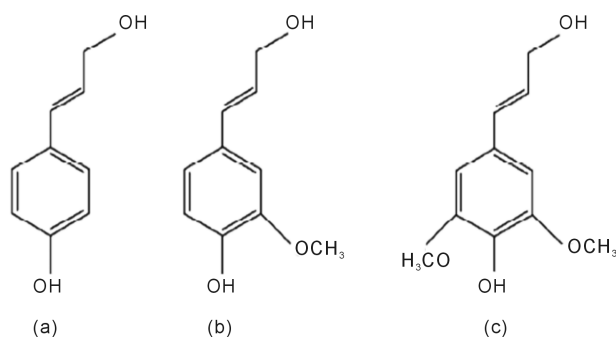


Figure 1. Structure units of lignin (a) p-coumaryl alcohol (b) guaiacyl (c) synapyl alcohol.

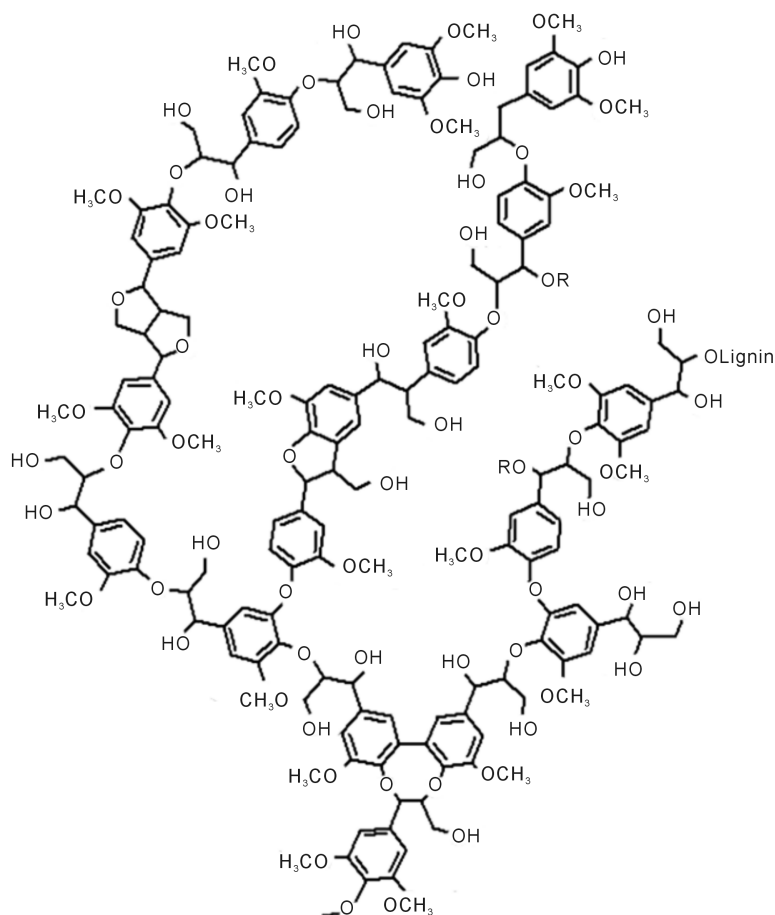


Figure 2. Three-dimensional structure of lignin polymer.

Lignin is obtained as a byproduct of the chemical pulping industry. Various types of industrial lignin are obtained. Among them sodium liginosulfonate (NaLS) obtained from the sulfite pulping process is a polyelectrolyte, which is soluble in water and a certain number of organic solvents. [16] [17]. To increase the potential applications of lignin in polymeric materials, some chemical modifications have been developed [18] [19], but these add stages to the process and/or raise their costs considerably. Therefore, the direct use of industrial lignin is the most favorable option because it is a relatively cheap raw material. Unmodified lignin has poor stability [20] and difficult melt processing [21], which make its direct use uncompetitive. However, many studies have focused on the incorporation of lignin in polymer materials by blending it with synthetic or other biobased polymers [22] [23] [24] [25].

6. Lignin Based Polyurethane Foam

6.1. Modified Lignin for PUF's

Lignin had been successfully modified by three chemical methods: hydroxymethylation, epoxidation, and phenolation. Through these three methods, the number of reactive functional groups of lignins had increased, and the impurity had decreased. Hydroxymethylation lignin was the second highest among phenolic hydroxyl groups, followed by epoxidation lignin. By adding modified lignin into PUF material, it could not only increase the decomposition temperature of the foam but also remarkably improve its mechanical properties. Besides, phenolic lignin, which contains the highest content of phenolic hydroxyl group, represents fine dispersion when generating blends with polyether glycol, and it was almost completely dissolved in the polyether glycol. By adding modified lignin into the polyether glycol and according to the mechanical properties of the obtained foam material and the decomposition temperature, the optimum amount of modified lignin could be achieved, that was, 1 wt% of phenolated lignin and 3 wt% of exoposidized lignin [26]. Crosslinking reaction of polyurethane foam based on lignin-aminated polyol was studied by FTIRATR spectroscopic analysis. It was shown from the results that the crosslinking reaction was approximated to be a first-order reaction [27]. The lignin-based rigid polyurethane (PU) foams were prepared by separately adding the refined alkali lignin and alkali lignin modified by 3-chloro-1,2-epoxypropane to be instead of 15% of the polyether glycol in weight. The mechanical performances of the prepared PU foams in the experiments were better than those of the commercial PU foam. Especially, the lignin PU foam modified by 3-chloro-1,2-epoxypropane had the highest glass transition temperature which was indicating that it had a better thermal stability and could be applied in the heat resistant field [28] [29].

6.2. Lignin with Other Biopolymer for PUF's

Lignin-based polyurethanes with elastomeric properties had been successfully synthesized using a chemical system consisted on lignin, 4,4'-methylene-diphenylene

diisocyanate (MDI) and polycaprolactone (PCL) of three different average-molecular weights (400, 750 and 1000) [30] also new types of PU foams derived from lignin and molasses were prepared. PU foams derived from this type of biopolymers could be used as insulation materials [31]. Combining lignin and castor oil as polyols for PU materials was promising [32] and also characterized PU materials based on sulfonated lignin and castor oil. The DMA results pointed out that the glass transition temperature of the samples increased and thus the degree of cross-linking with the increase of hydroxyl groups derived from different combinations of sulfonated lignin or sulfonated lignin oxypropylated or castor oil as polyols. Cinelli *et al.* [33] characterized flexible polyurethanes foams from liquefied lignin and two different chain extenders: castor oil and poly(propylene glycol) (PPG). The single use of unmodified or modified castor oil as a polyol is already consolidated [34]. Modified lignins had also been studied for this application [35] [36]. However, the combination of modified castor oil and unmodified industrial lignin showed an interesting opportunity for renewable and low cost polyols for preparation of PUF [37].

6.3. Biodegradable PUF's

Currently, the information concerning microbial degradation of commercial PU's in the environment is still limited. Lignin is a renewable material obtained in huge quantities as a by-product of the pulp industry. The ability of *A. niger* to degrade lignin based PU foams were studied in comparison with a conventional polyether-based one as control sample.

Lignin is generally described as highly resistant to biodegradation being mostly degrading by higher fungi via oxidative processes. Nevertheless, potential applications using lignin-degrading organisms and their enzymes have become attractive since they can provide both environmental friendly technologies for pulp and paper industry and added value to lignin-based products that can be presented as more degradable. Moreover, it had been recently reported that the incorporation of lignin at amounts lower than 10% (w/w) were able to increase biodegradability of commonly used polyurethanes [38] [39].

Thus, the incorporation of biobased structural units into the synthetic PU foams by using lignin-based polyols as a replacement of commercial ones could be an interesting strategy of producing a polymer susceptible to undergo easily microbial degradation, thus resulting in an enhanced biodegradability.

6.4. Flame-Retardant PUF's

Lignin, a natural macromolecule containing substantial aromatic rings and abundant hydroxyl groups, were firstly chemically grafted with phosphorus-nitrogen-containing groups via liquefaction-esterification-salification process to prepare lignin-based phosphate melamine compound (LPMC). And then the LPMC which had remaining hydroxyl groups were used to substitute parts of polyols and copolymerize with isocyanate to produce lignin-modified-PU foam

with excellent flame retardancy [40].

7. Benefit of Lignin in PU Foam (PUFs)

PUFs have accounted for two-thirds of the total PU demand in the literature [41] used for example in equipment manufacture, freeze sectors, aviation construction, and automotive production, and become an indispensable part of our daily living because of their light weight, good insulation, excellent corrosion resistance, and mechanical properties [42]-[48]. PUFs are usually inflammable and brittle. Therefore, it was indispensable to add certain retardant additives as compounds to improve their thermal and mechanical properties.

- It had been reported that PUFs blended with lignin displayed more excellent mechanical property and, at the same time, increased decomposition temperature, which also indicated that lignin-based PUFs could successfully replace currently used PUF materials on the market [49].
- There were two ways to add lignin into foam materials.
- One way was as an additive—lignin was added into foams directly.
- Another way was as a reaction agent—lignin was a substitute for a part of polyol to prepare PUFs [50] [51].

8. Conclusion

Lignin is an easily available, cost-effective and renewable biomaterial widespread in plants. Lignin is a byproduct of the paper industry, and exists in the black liquor of the pulping industry. Addition of lignin in the application of polyurethane not only is an effective method in using renewable biomass energy, but also enhances properties of polyurethane like excellent mechanical, heat-resistant and compression performance and aging-resistant performance [52]. The use of biobased raw materials can significantly contribute to sustainable development due to bio-degradability and low toxicity of the resulting products [53] [54]. At low concentration of lignin, the PU materials can be easily obtained, whereas it is difficult to get lignin-derived PU materials with high lignin concentration. Thus, complete replacement of lignin to polyol is a research focus [55].

9. Futuristic Research

Remarkable, from the practical point of view, further research on the compatibility between the lignin and the PU matrix should be enhanced. From the academic point of view, it is very necessary to probe functional mechanism of lignin with other additives in PU polymers, chemical modification of lignin and complete replacement of lignin to polyol will be a research focus.

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