# Preparation of Functionalized Kraft Lignin Beads

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**ABSTRACT:** Kraft lignin from black liquor wastes have been converted into epichlorohydrin-crosslinked beads by inverse suspension polymerization. A careful control of the different parameters allowed the preparation of spherical beads with a relatively narrow diameter size distribution. The obtained beads, without permanent porosity, swell well in hydroalcoholic media. Grafting of the sulfo-nylhydrazine moiety using a two-step route was further performed to apply them to carbonyl compounds scavenging. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1184–1189, 2010

**Key words:** Kraft lignin; functionalization of polymers; inverse suspension polymerization; swelling; waste

## INTRODUCTION

Lignin is the second most abundant, renewable macromolecule on earth after cellulose. It is found as a cell wall component in trees and other vascular plants, accounting for between 15 and 40% of the dry biomass matter in these plants. Lignin may be described as a random, amorphous, and complex three-dimensional polyphenolic network.[1] Hydroxyl groups and free positions on the aromatic rings determine mainly its reactivity and constitute the reactive sites to be exploited in macromolecular chemistry. However, lignin possesses other chemical functional groups, such as aliphatic hydroxyl and carboxylic groups. The relative amounts of the different functional groups depend on the botanic origin and on the extraction process applied.[2] In plants, lignin forms a three-dimensional network chemically bonded with cellulose by aryl–alkyl ether bonds and is not directly accessible without major chemical modifications of its native structure.[3] The main source of cheap separated lignin comes from the different processes employed in the pulp and paper industry to obtain cellulose.[4] Almost all the industrial plants presently in use in the world are running on the so-called Kraft process[5] that involves aqueous solutions of sodium hydroxide and sodium sulfite to extract cellulose by dissolution of lignin binding the cellulose fibres together in woody matrix. The major part of the degraded lignin biopolymer thus solubilised contributes to the dark brown pollution load of the so-called black liquors.[6] This very important amount of biomass waste, more than $10^7$ tons per year in the European Union alone, is at present merely used as in-house low-grade fuel.[7] Accordingly, lignin from black liquors represents a valuable source of renewable macromolecules for higher value applications.

We present here our results concerning the preparation of crosslinked lignin beads from black liquor coming from a Kraft paper plant and their functionalization for applications in scavenger chemistry.

## EXPERIMENTAL

### Materials

Lignin was separated from black liquor coming from a Kraft process plant (Smurfit, Facture Plant, France) using a published procedure.[8] Epichlorohydrin, 1,2-dichloroethane, Sorbitan monooleate (Span 80), and trimethylsilylchlorosulfonate were purchased from Aldrich and used as supplied.

### Suspension polymerization

In a typical experiment, lignin (22.5 g) was dissolved in 25 mL of a sodium hydroxide solution (2 mol $L^{-1}$), the solution (47 wt % of lignin) was stirred for 30 min at 50°C to ensure complete dissolution. A specially designed, three-necked, 1-Liter parallel-side flanged suspension reactor equipped with a double blade stirrer[9] was charged with the continuous

phase prepared by mixing the emulsifier, Span 80 (3 g), with 1,2-dichloroethane (400 mL, 500 g). The cooled lignin solution was then added to the reactor at room temperature. The mechanical stirring speed was adjusted (about 250 rpm) to obtain beads of satisfactory size. At this point, the crosslinking agent, epichlorohydrin, (4.2 g, 45 mmol) was added to the reaction vessel, and the solution was stirred for 30 min more. The temperature was then raised to 40°C and the two-phase system was stirred for 24 h. After cooling to room temperature, the reaction product was collected on a 0.18 mm sieve and washed thoroughly with tap water. Then a small quantity of coarse beads was removed on a 0.35 mm sieve. Overall, 20.6 g of black, smooth, spherical beads were collected (yield = 77%).

### Solvent beads swelling

Solvent swelling of the materials was measured using an ethanol/water mixture (12/88, v/v) adjusted to pH 3.5 with tartaric acid (4 g L$^{-1}$). Dry lignin beads (1 g) were placed in a 25 mL fritted graduated burette and dry bead volume was estimated ($V_0$). The swelling solution (5 mL) was then added, the beads gently stirred with a spatula and let at room temperature for 24 h. The swelled bead volume was then estimated ($V_S$). The $V_S$–$V_0$ value represents the swelling level (mL g$^{-1}$).

### Beads functionalization

Sulfonation

Lignin beads (1 g) were suspended in a dichloromethane solution (20 mL) of trimethylsilylchlorosulfonate (1.4 mL, 9 mmol). The suspension was gently stirred at room temperature for 24 h. The beads were then filtered and copiously washed with water, and then poured in a sulfuric acid solution (1 mol L$^{-1}$, 20 mL) for 48 h. The beads were filtered and copiously washed with water again and then dried under vacuum at 50°C for 24 h. Elemental S was assayed for loading determination. The SO$_3$H loading was 1.5 mmol g$^{-1}$.

Chlorination

Sulfonated lignin beads (3 g), were suspended in a DMF (20 mL) solution of thionyl chloride (5 equiv./SO$_3$H) for 18 h at room temperature. The beads were then filtered and washed successively with CH$_2$Cl$_2$ and THF, and then dried under vacuum for 24h.

Hydrazination

Chlorosulfonated lignin beads were added to an aqueous hydrazine hydrate solution (72 mmol, 4 equiv./SO$_3$H) in a water/ice bath. After stirring at 0°C for 5 h, the beads were filtered, washed with aqueous HCl (3 mol L$^{-1}$), then with water until pH > 5. After drying under vacuum, elemental N was assayed for loading determination. The SO$_3$NHNH$_2$ loading was 0.5 mmol g$^{-1}$.

### Characterization methods

Specific surface area determination

The specific surface area was determined by N$_2$ adsorption measurements performed on a Micromeritics ASAP 2010. The collected data were subjected to the Brunauer, Emmet, and Teller (BET) equation.[10]

Electron microscopy investigations

The morphology of the beads was observed by scanning electron microscopy (SEM) in a Hitachi TM-1000 microscope. Photographs were taken at several different magnifications between ×100 and ×10,000. Beads were mounted on carbon tabs, which ensured a good conductivity. A thin layer of gold was sputtered on the material fragments before analysis.

Beads size distribution

An average diameter was estimated for some samples from optical photographs after image processing with Scion Image freeware (Scion Corporation, Frederick, MA). The mean and the standard deviation were drawn by manual measurements of diameters from a population of at least 100 beads.

Elemental analysis

Elemental analyses were performed by the Service Central d'Analyses (Vernaison, France).

### RESULTS AND DISCUSSION

### Lignin bead preparation

After being solubilised in alkali solution by the breakage of its infinite lignocellulosic network because of the Kraft process, the damaged lignin from black liquor has to be crosslinked in order to regenerate a strong insoluble network. Phenolic molecules that possess unsubstituted aromatic positions can react at these positions with formaldehyde and form a network with trifunctional junctions. Therefore, the most studied application of isolated lignin was to replace, at least in part, phenol in phenol/formaldehyde resins (Novolac) and others thermoset polymers.[11] However, in the majority of the applications described, lignin is only a minor component of
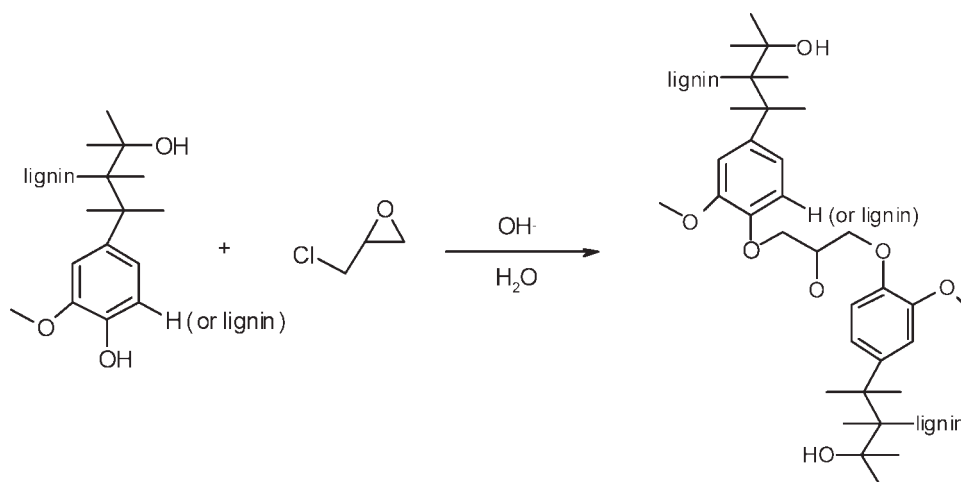
**Scheme 1** Crosslinking of Kraft lignin with epichlorohydrin.

the formulation, the main component remaining derived from fossil source. It was our aim, in this work, to prepare insoluble lignin networks in spherical shape (beads) using waste lignin from black liquor as the main component of the final material. For that, we decided to use epichlorohydrin as the sole crosslinking agent in minor quantities. Lignin-epoxy is a well-known compound used, in particular, in the fabrication of printed circuit boards.[12] To obtain modified, soluble lignin, the reaction is conducted using a large excess of epichlorohydrin.[13] In our case, we intended to obtain insoluble crosslinked materials; therefore, the experimental conditions had to be modified. Scheme 1 represents the crosslinking reaction of lignin with epichlorohydrin. The mechanism of the reaction of epichlorohydrin with phenol (a simplistic model of lignin) has been previously studied.[14] The reaction requires the participation of a mineral base (such as sodium hydroxide). It proceeds according to the following successive steps: (1) opening of the epoxide ring by the phenoxy ion giving access to 3-chloro-2-hydroxy-1-phenoxypropane intermediate (chlorohydrinphenyl ether); (2) dehydrochlorination of this intermediate product leading to phenylglycidyl ether; (3) reaction of a second phenoxy ion onto the oxirane ring giving the final product 2-hydroxy-1,3-diphenoxypropane (in the case of lignin, this step represents the crosslinking reaction). The authors have established that the reaction rates of steps 1 and 3 are of the same order of magnitude, whereas the reaction rate of step 2 is about three orders of magnitude greater. Therefore, it appears from these kinetic considerations that to obtain the generation of a satisfactory lignin network, the important parameters to adjust are: (1) a lignin concentration in the alkali solution as high as possible (saturated solution) to favour the crosslinking reaction (step 3) and, consequently, (2) a rather high alkali concentration both to ensure the dissolution of lignin by generation of a large amount of phenoxy ions and to favour step 2, and finally (3), a rather low value for the epichlorohydrin/lignin ratio, not to suppress step 3 in favour of step 1 (production of epoxidised lignin). A second reason to keep this value low is to limit the reaction between epichlorohydrin and the 3-chloro-2-hydroxy-1-phenoxypropane intermediate (epichlorohydrin oligomerization). The reaction temperature also plays an important role: the activation energies of steps 1 and 3 being close and higher than that of step 2, maintaining a rather low temperature (around 40°C) is expected to favour the production of crosslinked products.

**TABLE I**
**Results of the Crosslinking of Kraft Lignin with Epichlorohydrin in the Presence of NaOH in Suspension Polymerization**

| Entry | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Lignin mass (g) | 22.5 | 22.5 | 22.5 | 22.5 | 11.25 | 17 | 22.5 | 22.5 |
| Epichlorohydrin (mmol) | 45 | 45 | 45 | 45 | 22.5 | 34 | 45 | 45 |
| NaOH (mmol) | 25 | 40 | 50 | 50 | 50 | 50 | 50 | 50 |
| $H_2O$ (g) | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 |
| Reaction temperature (°C) | 40 | 40 | 40 | 20 | 40 | 40 | 30 | 50 |
| Beads yield (%) | 0[a] | 10[a] | 77 | 20 | 0 | 0[a] | 45[a] | 25[a] |

[a] Associated with abundant soluble lignin formation.

**TABLE II**
**Influence of Suspension Polymerization Parameters on Lignin Beads Morphology**

| Entry | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|
| Stirring speed (rpm) | 300 | 300 | 250 | 280 | 280 | 280 |
| Dispersed phase/continuous phase volume ratio | 1/5 | 1/8 | 1/4 | 1/8 | 1/8 | 1/8 |
| Beads yield % | 75 | 75 | 60 | 85 | 91 | 90 |
| Average beads diameter (μm) | 369 | 376 | 703 | 776 | 722 | 694 |
| Standard deviation (μm) | 7 | 5 | 9 | 11 | 10 | 6 |
| Sample size | 301 | 131 | 171 | 135 | 117 | 201 |
| Swelling in 12% v/v EtOH/water (mL·g$^{-1}$) | 1.10 | 1.25 | 1.20 | 1.10 | 1.10 | 1.40 |

Based on these kinetic considerations relative to the reaction of epichlorohydrin with phenol, we conducted a series of experiments on Kraft lignin to determine the optimal set of parameters to obtain insoluble lignin beads. The best way to obtain polymer beads of the desired size (100–800 μm) is suspension polymerization.[15] To achieve this, the alkali solution containing lignin has to be suspended in an inert, hydrophobic solvent containing a stabilizer. Our choice was 1,2-dichloroethane, a rather non-toxic solvent whose density ($d = 1.2$) closely matches that of the lignin alkali solution in order to facilitate bead formation using a low stirring speed. The chosen stabilizer was Span 80, often employed in reverse suspension polymerization.[16] Table I reports results of the different experiments conducted. Phenolic group content (1.96 mmol g$^{-1}$) and total hydroxyl group content (3.14mmol g$^{-1}$) of the starting Kraft lignin were determined according to a published procedure.[17] The epichlorohydrin/lignin ratio was set at about 2 mmol$_{(EP)}$ g$^{-1}$$_{(L)}$ for all experiments to favour a complete lignin crosslinking. Parameters varied were lignin and base concentrations. The stirring speed for all experiments reported in Table I was 300 rpm.

Experiment 1 was performed with the highest possible lignin concentration in alkali solution (47 wt %, saturated solution at 40°C), however, the results indicate the production of soluble modified lignin without formation of rigid beads: the hydroxide ion concentration ([OH$^-$] ~ 0.5 mmol g$^{-1}$) was not high enough to ensure rapid and total deprotonation of the aromatic hydroxyl groups. Increasing this value (entry 2, [OH$^-$] ~ 0.8 mmol g$^{-1}$) gave a low yield of beads. Good yield of large-sized beads was obtained with an even higher hydroxide ion concentration value (entry 3, [OH$^-$] ~ 1.0 mmol·g$^{-1}$). Entry 4 results indicate that there was no reaction at room temperature under the conditions used. Entries 5 and 6 clearly show that a reduced lignin concentration in the alkali solution (28 and 36 wt % respectively) resulted in the production of only soluble (noncrosslinked) lignin at 40°C. Entries 7 and 8 indicate that increasing or reducing the reaction temperature reduced the yield of insoluble lignin beads. Therefore, as postulated, these results point out that

both high lignin and high alkali concentrations are required to obtain lignin beads (entry 3).

A second series of experiments was then performed to study the influence of the suspension polymerization parameters (stirring speed and dispersed phase/continuous phase volume ratio) on the morphology of the resulting beads. Reaction parameter values are those of assay three (lignin concentration 47 wt %, [OH$^-$] ~ 1.0 mmol g$^{-1}$). Reaction temperature was maintained at 40°C for all assays. The corresponding results are reported in Table II.
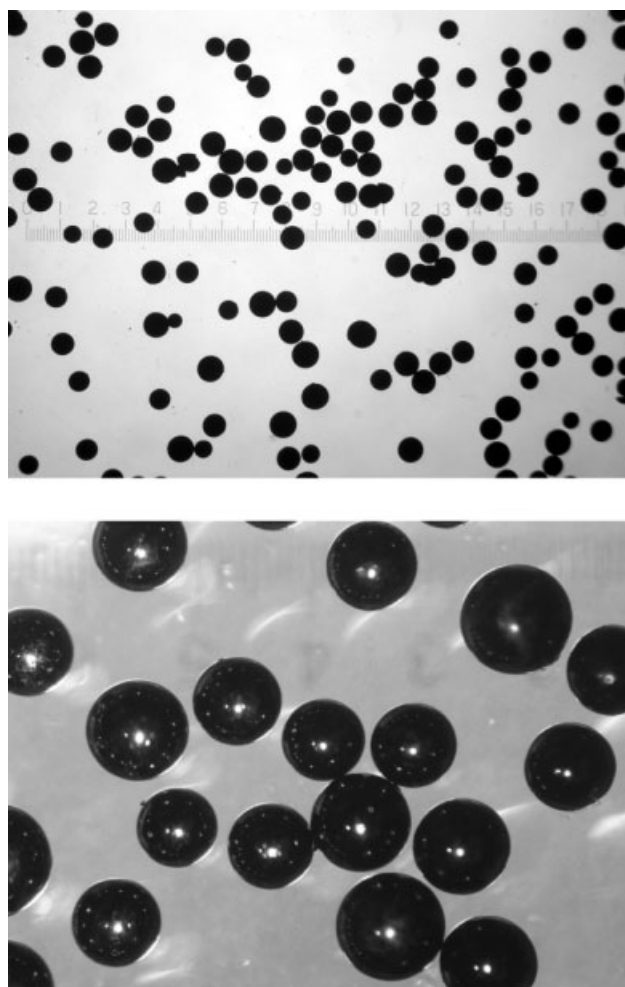


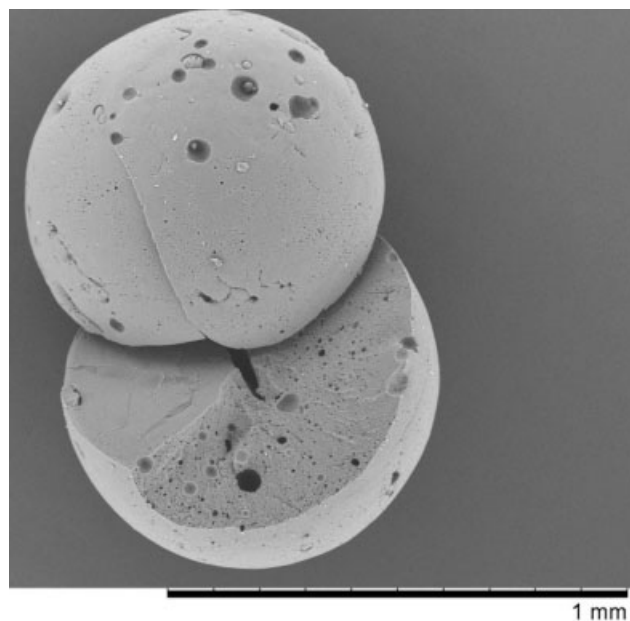**Figure 1** Optical images of lignin beads (Table II, entry 12).

**Figure 2** SEM micrograph of a lignin bead.

Entries 9 and 10 show that a conjunction of a rather high stirring speed with a diluted suspension medium gives good yields of beads of relatively small size. On the contrary, a more concentrated media with a lower speed results in a lower yield of larger beads (entry 11). Finally, the selection of a diluted media with a medium-range stirring speed resulted in reproducible high yields of beads of satisfactory size (entries 12–14). Figure 1 represents an optical micrograph of some beads from experiment 12. SEM analysis revealed that dry lignin beads possess a smooth surface and a compacted interior without any apparent porosity, excepted few large voids generated as a result of gas formation (Fig. 2). This behaviour was confirmed by a very low ($<1$ m$^2$ g$^{-1}$) specific surface area (BET).

## Crosslinking level estimation

Hydroxyl group content of the synthesized Kraft lignin beads was determined according to the same methodology as for starting Kraft lignin.[17] The average value obtained indicates a total hydroxyl group content of 1.45 mmol g$^{-1}$ and a phenolic content of 0.3 mmol g$^{-1}$. Considering that crosslinking with epichlorohydrin introduces a hydroxyl group when two phenyl group are consumed, these values, compared with those of the starting lignin, indicate an almost complete crosslinking on both kinds of hydroxyl groups.

## Solvent swelling

To be useful in scavenging applications these beads, having no permanent porosity, must present a certain swelling in solvents. Having in mind the expected use of these lignin beads for solid-liquid extraction in wine,[18] we estimated their swelling in an ethanol/water mixture (12/88, v/v) adjusted to pH 3.5, a model solution of this media. Swelling levels obtained are reported in Table II. The values obtained appear to be situated between those of gel-type, 2%-crosslinked beads (3.9 mL g$^{-1}$) and macroreticular, 8 %-crosslinked (0.7mL g$^{-1}$) polystyrenedivinylbenzene beads.[18]

## Lignin bead functionalization

Lignin beads were then functionalized according to Scheme 2.

Polymer-bound sulfonylhydrazine is an efficient scavenging agent for the removal of carbonyl compounds in organic[19] or aqueous media,[20] as well as for protein extraction.[21] The first step for the grafting of this scavenging moiety onto lignin beads is sulfonation on the free positions of the aromatic rings.
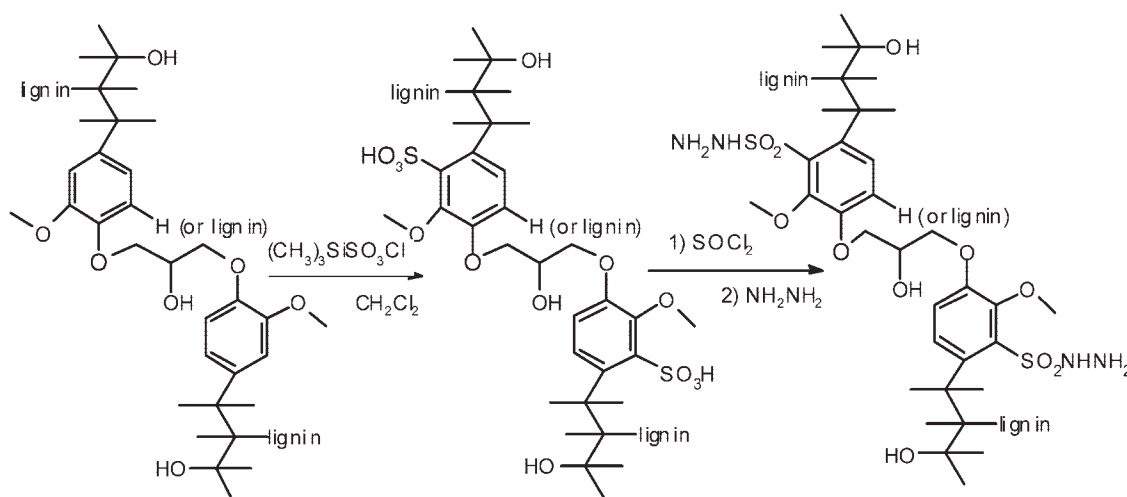


**Scheme 2** Functionalization of lignin beads.

The usual way to sulfonate polymer beads is by using concentrated sulfuric acid or chlorosulfonic acid[20] but, in the present case, use of both reagents conducted to the destruction of the lignin network. Therefore, lignin beads sulfonation was conducted under milder conditions using trimethylsilylchlorosulfonate according to a reported method.[22] The degree of sulfonation, as determined by titration, was about 1.5 $mmol_{(SO3H)}$ $g^{-1}$. The sulfonated beads were then treated with thionyl chloride then hydrazine hydrate to obtain the lignin grafted sulfonylhydrazine functions. The loading of the lignin beads was about 0.5 $mmol_{(SO_2NHNH_2)}$ $g^{-1}$.

## CONCLUSIONS

Kraft lignin beads containing a high lignin level (more than 80%) have been prepared through a straightforward method from black liquor wastes. Optimization of the reaction conditions allowed obtaining high yields of beads having a narrow size distribution. These beads of gel-type in nature, i.e. without permanent porosity, swell well in hydroalcoholic media. Grafting of sulfonylhydrazine moiety using a two-step route allows the potential application in carbonyl compounds scavenging.

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