Synthesis of Macroporous Monolithic Materials from a Waste Renewable Source

Claire Forgacz, Marc Birot, Hervé Deleuze

University of Bordeaux, Institut des Sciences Moléculaires, UMR-CNRS 5255, F-33405, Talence, France
Correspondence to: H. Deleuze (E-mail: h.deleuze@ism.u-bordeaux1.fr)

ABSTRACT: Interconnected porous monolithic materials can be directly obtained from non-templating methods by reacting raw Kraft black liquor with epichlorohydrin either in the presence or not of surfactant, whereas extracted lignin leads to non-porous materials. In the presence of a surfactant, micelles organization takes place and porosity of 40–60% can be achieved. Without surfactant, chemically induced phase separation occurs, giving materials with agglomerated nodules morphology. Carbonization followed by activation with CO_2 yield monolithic micro/mesoporous carbons with surface area of 300 m^2 g^{-1}. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41215.

INTRODUCTION

Today, trends toward conversion of wastes/biomass to valuable materials are growing stronger.[1] Industrial production of cellulosic chemical pulp from wood is widely made by Kraft pulping. In this process, lignin is dissolved and separated from the insoluble cellulosic pulp. The resulting aqueous solution containing inorganic and organic by-products is called black liquor.[2] Its composition depends on the raw material processed (i.e., softwood, hardwood or fibrous plant) as well as on the operational conditions of the pulping step. About half of the raw wooden material is dissolved in black liquor. In any case, black liquor is a complex, strongly alkaline aqueous solution containing organic biomass materials (degraded lignin, non cellulosic polysaccharides named hemicelluloses and resinous compounds of low molar mass) and inorganic compounds (mainly soluble ion salts).[3]

In modern pulp mills, the organic part of that liquor is used as low-grade fuel and the inorganic chemicals are recovered.[4] In recent years, attractive uses of industrial lignins, once separated from black liquors, have been reported for the preparation of high added-value chemicals.[5] However, the separation and purification of these starting materials are time and energy consuming and may preclude their full uses in renewable source-based materials,[6] even if efficient processes such as LignoBoost have been lately disclosed.[7]

Recently, we described macroporous interconnected monoliths from emulsion-templated Kraft black liquor.[8–10] Here, we present for the first time the preparation of macroporous organic materials, directly from industrial black liquor, where porosity is generated without emulsion templating or gas blowing methods. The natural polymers present in black liquor were crosslinked by reaction with epichlorohydrin to produce rigid monoliths after removal of water. This methodology was conducted either in the presence or absence of a non ionic hydrophilic surfactant. At last, pyrolysis under CO_2 was investigated in order to obtain monolithic activated carbon.

EXPERIMENTAL

Raw Materials

All chemicals were purchased and used as received: Triton^{TM} X-405 and Cremophor® EL (Sigma–Aldrich), epichlorohydrin (99%, Alpha-Aesar), sodium hydroxide (99%, Acros), lignin, (alkali, low sulfonate content 4% sulfur, Sigma–Aldrich, CAS 8068-05-1).

Industrial black liquor was provided by Smurfit Kappa (Cellulose du Pin plant, Biganos, France), where pine wood (*Pinus pinaster*) is almost exclusively used to make unbleached Kraft pulp. Samples of black liquor were taken out after the first evaporation step at the recovery plant. At this stage, its dry matter content after drying at 105°C is around 45 wt % and its viscosity at room temperature is 130 mPa s^{-1}. Most of the extractives (resinic acids, free fatty acids, fats, unsaponifiables) are removed from black liquor during the first stages of liquor regeneration.[11]

The characterization of black liquor was reported in our previous paper.[9] Thermogravimetric analysis of the dry matter

revealed that it contained around 40 wt % of inorganics. The Kraft lignin that was extracted from the black liquor by acidic precipitation represents 35–40 wt % of the dry matter.[12] The remaining organic matter, 20–25 wt % of the dry matter, is mainly composed of polysaccharides (hemicelluloses), and small amounts of extractives.[13]

Monoliths Preparation

Black liquor monoliths were prepared in five steps: (i) mixing at room temperature (30 min) epichlorohydrin with the crude black liquor and the surfactant if present (Triton[TM] X-405 or Cremophor® EL), (ii) pouring the mixture in cylindrical poly-tetrafluoroethylene moulds ($d = 4$ cm; $h = 3$ mm) then tightly sealed, (iii) crosslinking by thermal activation (60°C for 24 h) and, (iv) smooth removal of water and extractible compounds by ethanol in a Soxhlet, followed by drying of the monoliths in an oven (50°C) until constant weight.

The samples were codified as follows: for materials prepared with surfactant, Tri is for Triton[TM] X-405, Crem for Cremophor® EL, and the following digit indicates the mass fraction of surfactant used (e.g., Crem20 is a monolith prepared with 20 wt % of Cremophor® EL). For materials prepared without surfactant, M is for monolith, and the following number indicates the mass fraction of epichlorohydrin used (i.e., M6 is a monolith prepared with an epichlorohydrin mass fraction of 6%).

Carbonization and Activation

Monolithic sample M10 was pyrolyzed at a slow heating rate to preserve its geometric integrity (1°C min^{-1} from 25 to 600°C, plateau of 2 h at 600°C), under nitrogen atmosphere (200 mL min^{-1}). The pyrolyzed monolith was then activated under a carbon dioxide flow (200 mL min^{-1}), at a heating rate of 1°C min^{-1} from 25 to 600°C followed by a plateau of 2 h at 600°C. The final yield of activated carbon M10-carb was 40 wt %.

Characterization

The effective open porosity (P), bulk density (d_b) and the connection size distribution of each sample were determined by mercury intrusion porosimetry using a Micromeritics Autopore IV 9500 porosimeter with the following parameters: contact angle = 130°, mercury surface tension = 485 dyne cm^{-1}, maximum intrusion pressure = 124 MPa. The reported connection size is the average pore diameter ($4V/A$) where V is the total intrusion volume and A the calculated total pore area. The skeletal density d_s of the foams can be estimated from the equation:

$$\frac{P}{100} = 1 - \frac{d_b}{d_s}$$

The specific surface area was determined by N_2 adsorption measurements performed on a Micromeritics ASAP 2010. The samples (100–120 mg) were degassed for 30 h at 160°C under vacuum (1–2 Pa) prior to analysis. The collected data were subjected to the Brunauer, Emmett, and Teller (BET)[14] and t-plot[15] treatments.

The morphology of the monoliths was observed by scanning electron microscopy (SEM) in a Hitachi TM-1000 microscope. Photographs were taken at several different magnifications between ×1,000 and ×10,000. Pieces of monoliths (section of about 0.5 cm^2) were mounted on a carbon tab and a thin layer of gold was sputtered on the fragment prior to analysis (coating current 5 mA, time 120 s). An average nodules diameter was estimated from SEM micrographs after image processing with ImageJ freeware (NIH, USA) from a population of at least 150 nodules. To get a better estimation of the real diameter, a statistical correction was introduced by multiplying the observed average value by a factor $K = 2/(3^{1/2})$.[16] Analytical statistics were used to determine the volume average diameter $D_{4,3}$ and the uniformity factor U.[17]

Thermogravimetric analyses were performed on a Netzsch STA 409 thermobalance under N56 argon flow. The heating rate was 10°C min^{-1}, and the temperature ranged from 25 to 1000°C. Elemental analyses were performed by the Service Central d'Analyses (Vernaison, France).

RESULTS AND DISCUSSION

We have previously reported the preparation of foams from emulsion-templated Kraft black liquor by crosslinking with epichlorohydrin[9,10] (Figure 1). However, others approaches may be followed to obtain porous monolithic materials from an aqueous solution of precursor. It is well established that the polymerization of hydrophilic monomers in the confinement of lyotropic liquid crystalline phases of nonionic surfactants produces gels with variable pore architecture of hundreds of nanometer to micrometer size range.[18] This approach has recently been applied to the preparation of guar-based hydrogels.[19] Therefore, we decided to investigate the behavior of the black liquor when using this methodology.

Materials Prepared with Surfactants

To study the effect of surfactants on the morphology of the monoliths, a series of material was prepared by changing the nature and the amount of surfactant. The two surfactants previously used to make emulsion-templated porous monoliths[9] were selected: Triton[TM] X-405—polyoxyethylene (40) isooctylphenyl ether, HLB = 17.6—and Cremophor® EL—polyethoxylated (35) castor oil, HLB = 12–14 –. The epichlorohydrin mass fraction was fixed at 10% and the amount of surfactant was varied from 8 to 30 wt %. The different samples were codified as follows: Tri is for Triton[TM] X-405, Crem for Cremophor® EL.
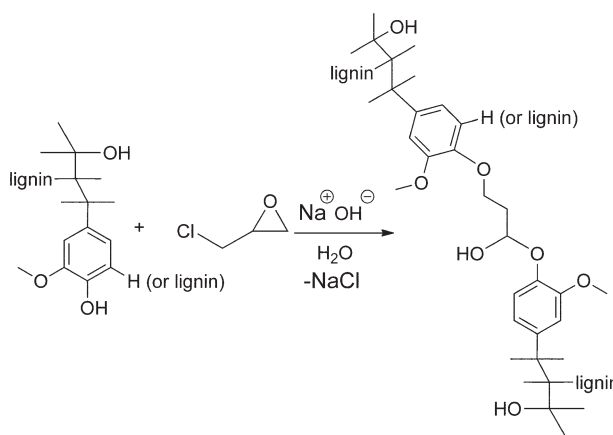

Figure 1. Crosslinking of Kraft lignin with epichlorohydrin.
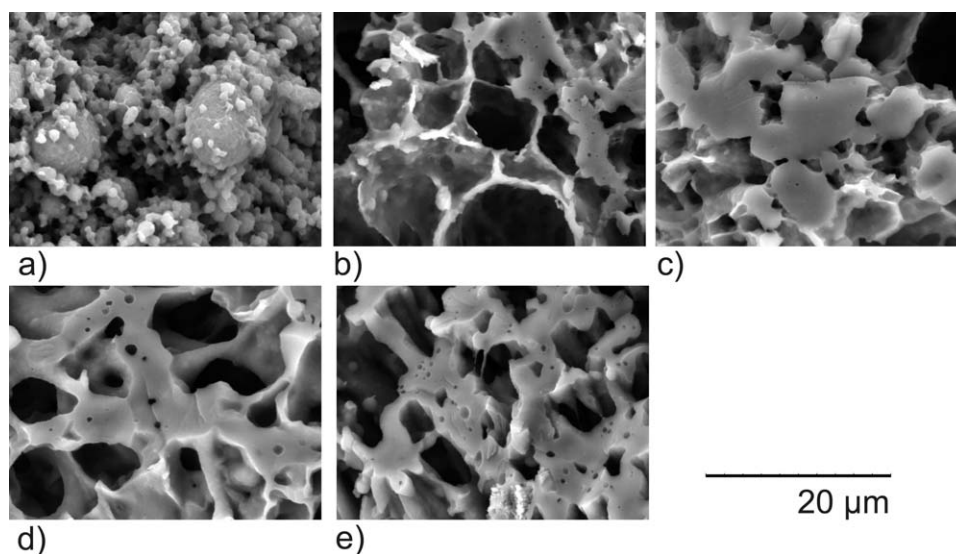
Figure 2. SEM micrographs of Tri8 (a), Tri15 (b), Tri20 (c), Tri25 (d), and Tri30 (e) samples.

The following digit indicates the mass fraction of surfactant used. For example, Crem20 is a monolith prepared with 20 wt % of Cremophor® EL.

The morphologies of the different samples prepared examined by SEM are presented in Figures 2 and 3. Their porous characteristics are reported in Table I.

For samples prepared with Triton™ X-405, the total open porosity is almost constant, around 40%. The average pore diameter value falls between 0.5 and 1.5 μm. It increases with the amount of Triton™ X-405 used, while the aspect of the walls of the foam changes gradually from nodular to smooth until the collapse of sample Tri30 (Figure 2).

For samples prepared with Cremophor® EL, the behavior is different. From Crem8 to Crem30, the total open porosity increases and the average pore diameter decreases. At low level of surfactant [<15%, Figure 3(a,b)], agglomerated microspheres are observed on the walls of the monoliths. Above 20% of Cremophor® EL [Figure 3(c–e)], an open cell morphology with cell walls thickening is arising.

The changes in the morphology of the materials with the concentration of surfactant are probably due to variations in the organization of the surfactant phase. The fact that Triton™ X-405 does not contribute to the porosity suggests that, because of its high HLB value, it stabilizes the growing network that becomes more hydrophobic as epichlorohydrin reacts with hydroxyl groups of lignin. In the case of Cremophor® EL, which is less hydrophilic with a lower HLB value, micelles organization seems responsible for the formation of the pores in between the growing network.

For all samples, prepared either with Triton™ X-405 or Cremophor® EL, the calculated skeletal density d_s is in the range 1.4–1.6, similar to the values obtained by helium
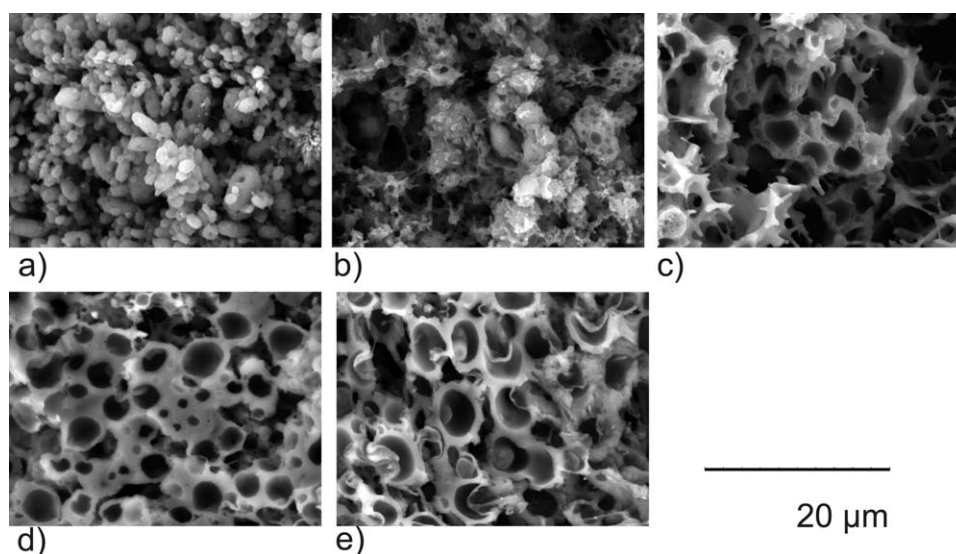

Figure 3. SEM micrographs of Crem8 (a), Crem15 (b), Crem20 (c), Crem25 (d), and Crem30 (e) samples.

Table I. Mercury intrusion Characteristics of Monoliths Prepared in the Presence of Surfactant (Averaged from 2 Measurements)

| Sample	Open porosity (%)	Bulk density d_b (g cm^{-3})	Skeletal density d_s (g cm^{-3})	Average pore diameter (4V/A) (µm)
Tri8	40 ± 1	0.90 ± 0.02	1.51 ± 0.04	0.50 ± 0.06
Tri15	44 ± 1	0.83 ± 0.03	1.49 ± 0.03	0.90 ± 0.09
Tri20	42 ± 1	0.87 ± 0.02	1.51 ± 0.03	0.70 ± 0.07
Tri25	40 ± 1	0.88 ± 0.01	1.52 ± 0.01	1.50 ± 0.40
Tri30	36 ± 1	0.99 ± 0.02	1.55 ± 0.02	0.65 ± 0.04
Crem8	48 ± 1	0.81 ± 0.01	1.59 ± 0.01	0.45 ± 0.06
Crem15	47 ± 1	0.73 ± 0.03	1.37 ± 0.05	0.42 ± 0.01
Crem20	48 ± 1	0.76 ± 0.03	1.45 ± 0.05	0.21 ± 0.06
Crem25	65 ± 3	0.50 ± 0.04	1.46 ± 0.06	0.18 ± 0.05
Crem30	65 ± 3	0.49 ± 0.05	1.40 ± 0.04	0.25 ± 0.06

Figure 4. Example of monoliths prepared from black liquor and epichlorohydrin (same formulation sample M10). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pycnometry for the foams made by emulsion-templating,[9,10] and to the true density of Kraft lignin. These results indicate that no additional closed porosity is present.

Materials Prepared Without Surfactant

Another way to generate porosity during the crosslinking of functional polymeric chains in solution is chemically induced phase separation (CIPS).[20] In that case, crosslinking, by reducing the solubility of the polymeric chains, induces the formation of polymer-rich and solvent-rich phases that lead finally to a solvent-filled monolith.

To determine the influence of the amount of crosslinking agent (epichlorohydrin) on the morphology of the final materials obtained through this approach, three materials were prepared from crude black liquor with 6, 10, and 20 wt % of epichlorohydrin. They are codified as follows: M is for monolith, and the following number indicates the mass fraction of epichlorohydrin used. For example, M6 is a monolith prepared with an epichlorohydrin mass fraction of 6%.

After washing and drying, the different monoliths prepared (M6, M10, and M20), appear as light-brown, self-sustaining blocks (Figure 4). Helium pycnometry measurements reveal a skeletal density of these materials of 1.5 ± 0.1 g cm^{-3}.

Figure 5 shows SEM micrographs of the different monoliths made from crude black liquor. All samples display a macroporous structure constituted of agglomerated small particles, the pores being voids between these nodules. We must mention at that point that purified Kraft lignin handled in the same conditions [ML10, Figure 5(d)] gives materials having no permanent porosity, but that swell in solvent,[21] like styrene/divinylbenzene gel-type resins.[22] The morphology of our materials [Figure 5(a–c)] can be related with that obtained when styrene and divinylbenzene are copolymerized in the presence of a non-solvating porogen, leading to macroporous resins.[22] Black liquor is a complex alkaline medium constituted, for one part, of lignin chains acting as polyelectrolyte with broad molecular size distribution.[23] At black liquor pH (pH > 13), the phenolate groups
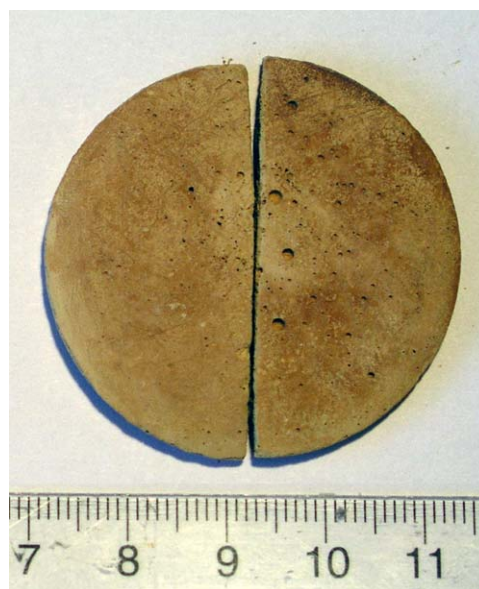
are completely ionized and the chains are soluble under a spherical, compact shape. On the other hand, hemicelluloses, the second major organic component of black liquor, are branched polysaccharides that tend to form loose expanded random coils.[4] Chemically induced phase separation (CIPS) occurs during crosslinking: lignin chains, progressively linked together through epichlorohydrin bridges, become less soluble in the aqueous media, due to the lowering of phenolate ions contribution.[24] Therefore, nodules of agglomerated lignin appear. The surrounding liquid media, constituted of an aqueous solution of hemicelluloses chains, plays the role of a polymeric porogen.[25] In that case, it is expected only a broad distribution of macroporous voids in between the agglomerated nodules.

Thus, it appears that the amount of crosslinking agent plays a role on the nodules size by controlling the kinetics of the phase separation. The average microspheres size of samples M6, M10, and M20 was determined by image analysis (Table II). When the amount of epichlorohydrin is high (M20), small monodisperse nodules are formed with an average diameter of 1.9 µm and a uniformity factor $U = 0.18$. Together, the average pore diameter is small (1.6 µm). With a lower level of epichlorohydrin (M10), the nodules size is larger (3.2 µm), with a broader distribution ($U = 0.87$) and a larger pore diameter (3.1 µm). Sample M6, crosslinked with the lowest epichlorohydrin ratio, displays an average nodules diameter value of 2.6 µm, lower than expected, which is probably due to partial collapse of the growing network.

Mercury intrusion porosimetry analyses (Table II) agree with the SEM observations. Intrusion vs. pressure curves (Figure 6) indicates a good penetration of mercury into the porous matrix, though for M6 sample some compression can be observed. This behavior may be attributed to the low crosslinking level used in that case. In addition, sample M6 shows a low porosity (45%)
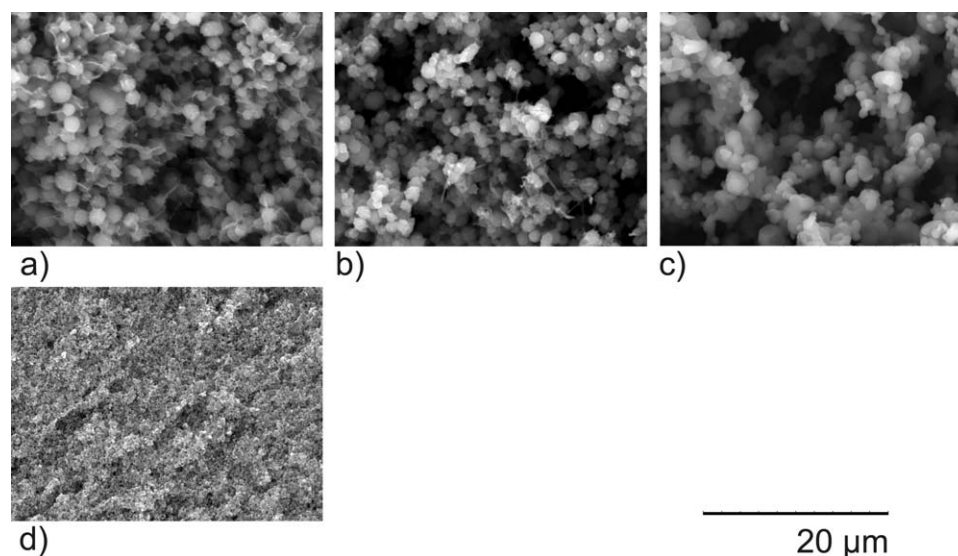
Figure 5. SEM micrographs of M6 (a), M10 (b), M20 (c), and ML10 (d).

associated with a low average pore diameter (400 nm). This result demonstrates the partial collapse of the internal structure, as supposed above. Sample M10, crosslinked with 10 wt % of epichlorohydrin, gets pore diameter double that of M20, crosslinked with 20 wt % of epichlorohydrin, but this does not affect the open porosity of the materials situated around 65%. In both cases, it is higher than expected from the sole removing of water initially present in black liquor (55 vol %, assuming an aqueous phase density of 1 g mL^{-1}). This means that part of the matter contained in the black liquor (mainly inorganic matter and small organic compounds) is not crosslinked by epichlorohydrin and is extracted during the washing step of the monoliths.

At a constant level of crosslinking epichlorohydrin (10%), it must be noted that the porosity of M10, prepared without surfactant, is higher than that of the Trix series. It is comparable to that of Crem25-Crem30 materials, but with an average pore diameter ten times larger (Table I). In addition, SEM micrographs [Figures 2(d,e) and 4(b)] reveal that their morphologies are totally different.

Thermal Treatment: Preparation of Activated Porous Carbon
Activated monolithic carbons with high specific surface area are susceptible to find numerous applications like gas or water

purification, selective adsorption or heterogeneous catalysis.[26] Kraft lignin is known to be a starting resource to prepare these carbons.[27] However, the resulting materials are micro/mesoporous powders with little, if any, large macroporous volume. We were interested to study if activated carbonization could generate some microporosity in the material walls of our black liquor-derived macroporous monoliths. Therefore, we conducted a pyrolysis under nitrogen followed by a physical activation under carbon dioxide atmosphere on sample M10.

Carbonization caused a significant volume shrinking (45–50%) but preserved the global shape of the piece of material. However, the open macroporosity analyzed by mercury intrusion remained almost unchanged (Table II). Only a small reduction of the average pore diameter could be noticed.

SEM micrographs of the sample before and after activated carbonization are reported in Figure 7. The internal structure of the monoliths appears not affected by activated carbonization, but partial fusion of the nodules seems to have occurred, due to
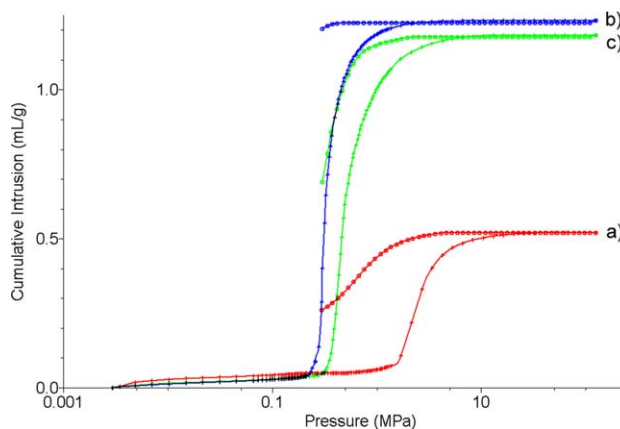
Table II. Characteristics of Monoliths Prepared Without Surfactant

Sample	Open porosity[a] (%)	Average pore diameter ($4V/A$)[a] (µm)	Microspheres size[b] (µm)	U
M6	45 ± 1	0.40 ± 0.01	2.6	0.73
M10	65 ± 1	3.10 ± 0.20	3.2	0.87
M20	63 ± 1	1.60 ± 0.05	1.9	0.18
M10-carb	65 ± 2	2.50 ± 0.30	–	–

[a] From mercury intrusion data (averaged from three measurements).
[b] Volume average diameter $D_{4,3}$ from SEM image analysis.

Figure 6. Mercury intrusion/extrusion curves for samples (a) M6; (b) M10; and (c) M20. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
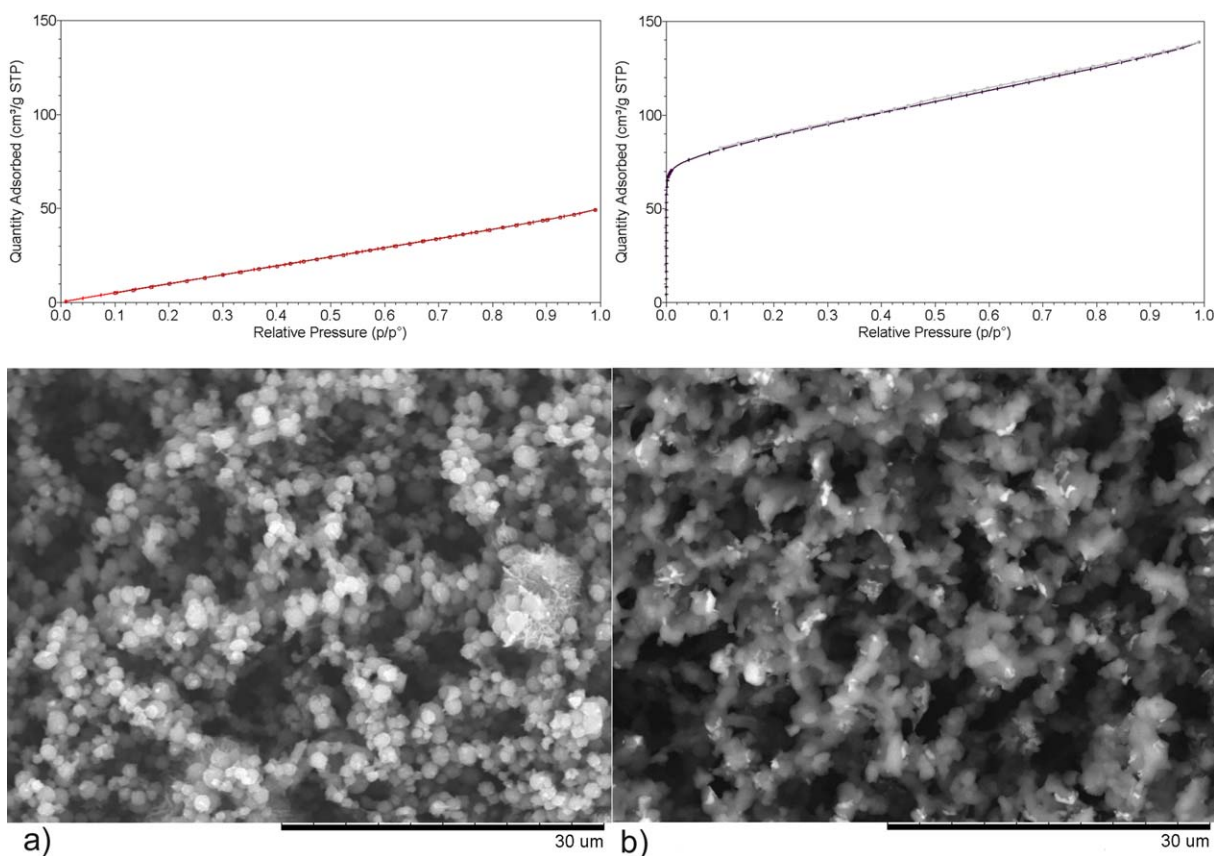
Figure 7. SEM micrographs and nitrogen adsorption isotherms of the original M10 (a) and carbonized M10-carb (b) samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the reorganization of the matter during this step [Figure 7(b)]. This is why no data is given for the microspheres size of sample M10-carb Table II.

The adsorption isotherm of sample M10 [Figure 7(a), left] revealed a structure with weak gas/solid interactions (type III isotherm). The adsorption isotherm of the carbonized sample M10-carb [Figure 7(b), right] appeared as a type I/II hybrid. Micropores are filled first, and then mesopores are filled gradually. Specific surface area (BET) and pore volumes are reported in Table III. The specific surface area (BET), rises from 74 to 318 $m^2 g^{-1}$ and the total pore volume rises from 0.08 to 0.21 $cm^3 g^{-1}$. Thus, the black liquor-derived monolith leads to micro/mesoporous activated carbon after activation under CO_2 atmosphere.

Table III. N_2 Sorption Data of Monoliths Before and After Carbonization

Sample	Specific surface area[a] ($m^2 g^{-1}$)	Single point total pore volume[a] ($cm^3 g^{-1}$)	External surface area[b] ($m^2 g^{-1}$)	Micro/mesopore volume[b] ($cm^3 g^{-1}$)
M10	74	0.08	–	–
M10-carb	318	0.21	25	0.17

[a] From BET treatment of N_2 adsorption data.
[b] From t-plot treatment of N_2 adsorption data.

CONCLUSIONS

Black liquor, a renewable by-product of the papermaking industry, can be converted directly into porous monolithic solids by cross-linking lignin contained in it with epichlorohydrin in the presence or not of surfactant. With surfactants, the open macroporosity of the monoliths is 40–65%, with pore size of 0.2–1 μm. The concentration of the surfactant influences its organization, hence affects the morphology of the materials. Nodules are formed at low level, while a cellular structure is observed at higher amounts. Without surfactant, chemically induced phase separation occurs during the crosslinking reaction, whereas purified lignin leads to non-porous materials. The materials obtained exhibit higher open macroporosity and pore size than those prepared with surfactant. Their morphology is nodular, the sizes of the nodules and of the pores being related to the amount of epichlorohydrin. Activated carbonization under CO_2 transforms the solid into a micro/mesoporous carbon monolith with a specific surface area of 300 $m^2 g^{-1}$, while preserving an open macroporosity of 65%.

ACKNOWLEDGMENTS

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