

Synthesis of Porous Emulsion-Templated Monoliths from a Pulp Mill By-Product

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ABSTRACT: Black liquor is a by-product of the paper mill Kraft process that deserves more valorization than its present use as low-grade fuel. In this work, we present an original approach allowing the preparation of macroporous interconnected monolithic materials using as-received black liquor as main raw material. The process involves the formulation of an oil-in-water medium internal phase emulsion as soft templating porosity medium. The oil (internal phase) used is castor oil, whereas the continuous phase is constituted of black liquor containing a hydrophilic surfactant and epichlorohydrin as lignin crosslinking agent. Due to the high viscosity of the system, a specially designed emulsifying device was employed. The proper choices of the surfactant and emulsification conditions allow obtaining cellular biopolymers with almost monodisperse, interconnected void structure and satisfactory mechanical properties. These innovative results are promising for the future development of fully bio-based emulsion-derived materials. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2606–2613, 2013

KEYWORDS: emulsion polymerization; porous materials; cellulose and other wood products; biopolymers and renewable polymers; colloids

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INTRODUCTION

Because of depletion of natural resources, increasing greenhouse emissions and awareness of the need for sustainable development, the trends toward transformation of wastes/biomass to valuable materials is growing stronger.¹ Kraft pulping is the most widely used process in the industrial production of cellulosic chemical pulp from wood. During the Kraft process, lignin is degraded and dissolved almost completely, and thus separated from the insoluble cellulosic pulp. The resulting aqueous solution containing the inorganic and organic by-products of the process is called black liquor.² Its chemical composition depends on the type of raw material processed, i.e. softwoods (such as pine), hardwoods (e.g., eucalyptus) or fibrous plants (like bamboo), as well as on the operational conditions of the pulping stage.³ However, in any case, black liquor can be considered as a complex, strongly alkaline aqueous solution, containing organic biomass materials (lignin, noncellulosic polysaccharides called hemicelluloses and resinous compounds of low molar mass) and inorganic compounds (mainly soluble ion salts).⁴

In chemical pulp mills, about half of the original raw wood material is dissolved in black liquor. In modern pulp mills, the organic content of that liquor is used as low-grade fuel and the inorganic chemicals recovered.³ Recently, several more attractive

uses of industrial lignin contained in black liquor have been reported for the preparation of high added-value chemicals after their extraction and separation.⁵ However, the separation and purification processes needed to obtain these starting materials are time and energy consuming and may preclude their full uses in materials,⁶ even if more efficient procedures such as the LignoBoost process have been recently disclosed.⁷

Emulsion templating is a simple and versatile method for the preparation of highly interconnected microcellular materials (void size range 2–100 μm , interconnections diameter 0.5–2 μm) by polymerizing the continuous phase of a High Internal Phase Emulsion (HIPE).⁸ The obtained materials have been named polyHIPEs by Unilever researchers.⁹ The historic polyHIPE preparation involves the formation of a stable, water-in-oil concentrated emulsion using hydrophobic monomers as part of the continuous phase (most generally a mixture of styrene and divinylbenzene with, optionally, the addition of a functionalized styrene such as 4-vinylbenzyl chloride) and an aqueous phase as the dispersed phase. A great deal of work has been devoted to the study of this particular system.^{10–16} The main topics studied have been the good control of the porous morphology (voids and interconnecting windows size dispersion),^{17–22} and attempts to increase the mechanical strength of the material which, in its native

formulation, is usually considered as insufficient for practical applications.^{23–26}

Numerous efforts have also been devoted to the use of hydrophobic (meth)acrylate derivatives.^{27,28} Much less work has been published on the synthesis of polyHIPE based on hydrophilic (i.e., water-soluble) monomers emulsified by a hydrocarbon.^{29,30} Very though polyHIPEs materials from N-rich heterocyclic monomers have also been reported.^{31,32} Barbetta et al. prepared gelatin- and dextran-methacrylate polyHIPE scaffolds using an oil-in-water concentrated emulsion.^{33,34} Blaker et al.³⁵ disclosed recently the preparation of renewable nanocomposites from water-in-acrylated soybean oil emulsions stabilized by hydrophobized bacterial cellulose.

Until recently, it was generally admitted that polyHIPEs were expected to have an open-cell morphology only for a close packed structure of monodisperse droplets (dispersed phase volume fraction $\phi > 74\%$ of the total emulsion),^{36,37} the number of connecting neighbors (coordination number) for a given droplet of the internal phase being, in that case, 12. Inversely, geometrical considerations allow determining that a regular tetrahedral monodisperse packing is obtained with $\phi \approx 34\%$, each sphere having four touching neighbors.³⁸ In practice, packing of droplets of the inner phase of a concentrated emulsion is probably more accurately represented by a random packing scheme where there is no long-range order. Random close packing of monodisperse hard spheres occurs at a packing fraction of $\phi \approx 64\%$ with a coordination number of 6,³⁹ whereas random loose packing of these spheres, i.e., the minimal packing fraction still allowing some contact between adjacent spheres, has been estimated by computational modeling to occur at $\phi \approx 55\%$, with a coordination number of 4.⁴⁰ All these considerations allow to expect that concentrated emulsions with a dispersed phase fraction lower than 74% still give access to interconnected cellular polymers (although with a lower coordination number for the void cavities), as it is generally believed that interconnections form at droplets contact area during the curing phase.⁴¹ This has been experimentally confirmed by Bismarck et al. in a seminal work⁴² where it has been clearly established that emulsion-templated materials prepared from Medium Internal Phase Emulsions (MIPE, $34\% < \phi < 74\%$) possess a somewhat interconnected porous structure, as demonstrated by permeability measurements.

It was our aim in this work to prepare, for the first time, emulsion-templated monoliths using a renewable reagent such as black liquor as the main raw component. The objective was to obtain bio-sourced monoliths having an interconnected porous structure with acceptable mechanical toughness.

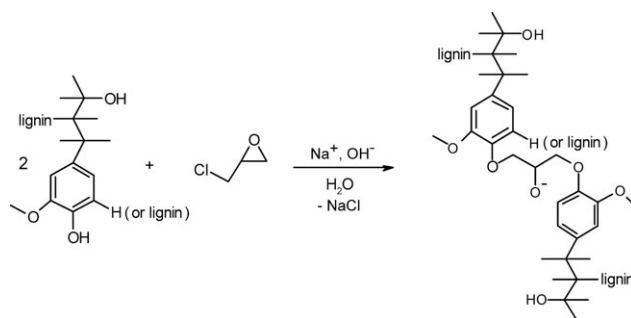
EXPERIMENTAL

Materials

Black liquor (45 wt % dry matter) coming from a Kraft paper mill (Smurfit Kappa Cellulose du Pin, Biganos, France) was used as received. TritonTM X-405, Cremophor[®] EL, epichlorohydrin, and castor oil were purchased from Aldrich. All chemicals were used as received.

Black Liquor Analysis

The as-received Kraft black liquor comes as a viscous, black liquid. Its physico-chemical properties are as follows: dynamic



Scheme 1. Crosslinking of Kraft lignin with epichlorohydrin.

viscosity $\mu = 7000$ mPa s at 23°C; pH = 14 (solution diluted to 5% dry matter); density $\rho = 1.3$ g mL⁻¹; dry matter amount = 45 wt %. Phenol group content (0.5 mmol g⁻¹) and total hydroxyl group content (0.8 mmol g⁻¹) of black liquor were determined according to a published procedure.⁴³

Black Liquor Cross-Linking

After being solubilized in alkali solution by the breakage of native infinite lignocellulosic network during the Kraft process, the damaged lignin contained in black liquor has to be cross-linked in order to regenerate a strong, insoluble network. Phenolic molecules that possess non-substituted aromatic positions can react at these positions with formaldehyde to form a network. Therefore, the most studied application of isolated lignin is to substitute phenol in phenol/formaldehyde resins and others thermoset polymers.⁴⁴ Epichlorohydrin is another crosslinking agent in use in the synthesis of lignin-epoxy, a compound involved in the fabrication of printed circuit boards.⁴⁵ Furthermore, epichlorohydrin can be seen, in some way, as an upcoming biosourced monomer being produced from glycerol by the newly developed Solvay Epicerol process.⁴⁶ Therefore, we decided to use epichlorohydrin as sole crosslinking molecule in this work. Scheme 1 represents the crosslinking reaction of lignin with epichlorohydrin. In a previous study,⁴⁷ we have established that, to obtain a satisfactory network, the important parameters to adjust are: i) a lignin concentration in the alkali solution no lower than 40 wt. % in order to favor the crosslinking reaction and, ii) a rather high alkali concentration to ensure lignin dissolve by generation of a large amount of phenoxy ions. Both conditions are fully completed with the 45 wt. % black liquor used in this work.

Formulation of Stable Castor Oil-in-Black Liquor Concentrated Emulsions

Black liquor being an aqueous solution, the dispersed phase of the concentrated emulsion has to be hydrophobic. In order to avoid the use of organic solvents, we opted for a vegetable oil: castor oil, mainly constituted of triglyceric esters of ricinoleic acid, a C₁₈-hydroxylated unsaturated fatty acid. This oil cumulates the advantages to be soluble in ethanol, which will simplify its extraction from the final monoliths, and to be more dense and more viscous than any other common vegetable oil ($d = 0.955$ g mL⁻¹; $\mu = 950$ mPa s). These values being comparable to those of the black liquor, the emulsification process will be eased.

The choice of the surfactant is critical for the formation and the stability of a concentrated emulsion. Several nonionic surfactants with a hydrophilic-lipophilic balance (HLB) value between 15 and 20 (generally employed for oil-in-water emulsions production) were tested in order to obtain stable emulsions: polyoxyethylene (20) sorbitan monolaurate (Tween[®] 20), polyoxyethylene (20) sorbitan monooleate (Tween[®] 80), polyoxyethylene (20) oleyl ether (Brij[®] 98), polyoxyethylene (40) nonylphenyl ether (Igepal[®] CO-890), octylphenol ethoxylate, Triton[™] X-405, and Cremophor[®] EL. In preliminary experiments, hand-made emulsions were prepared in a mortar using these different surfactants (5 wt % of the continuous phase), with a weight fraction of oil inserted in the emulsion of 55 wt %. The stability of the emulsions was appreciated by visual observation of any creaming after 24 h standing at room temperature. Satisfactory results were obtained only with Triton[™] X-405 and Cremophor[®] EL that were solely used in the following of this work. Triton[™] X-405 is a polyoxyethylene (40) isooctylphenyl ether hydrophilic surfactant (HLB = 17.6) previously used in polyHIPE preparation.^{48,49} Cremophor[®] EL is a polyoxyethyleneglycerol triricinoleate (35) derived from castor oil (HLB = 12–14).⁵⁰

HIPE Preparation

In a typical experiment, black liquor (20 g), Cremophor[®] EL (0.8 g), and epichlorohydrin (2.0 g, 21 mmol) were placed in a test tube. The mixture was homogenized at room temperature using a vortex. Emulsification was performed using a laboratory-made system already described.^{25,47} Briefly, this device is composed of two polypropylene syringes (50 mL, internal diameter (*ID*) = 28 mm) connected with a small-section tube (*ID* = 4 mm, *L* = 20 mm). The aqueous components of the emulsion (about 18 mL) were put into one of the syringes and castor oil (22 mL) was added. The second syringe was connected to the first one using the connecting small tube. This system was then adjusted in the “two-syringe” emulsification device and the emulsion was formed by the backwards and forwards motion of the syringe plungers. The rate of passage of the emulsion through the connecting tube was adjusted to 10 min⁻¹. The emulsification time was 30 min.

Monoliths Preparation

The obtained thick, black emulsions were placed in tightly closed PTFE cylindrical moulds of different sizes and cross-linked for 48 h at 60°C in an oven. The resulting monoliths were extracted by refluxing with ethanol (48 h) in a Soxhlet apparatus and dried in a vacuum oven at room temperature to constant weight.

Characterization of the Monoliths

Porosity Determination. The porosity ϕ_{exp} and the pore size distribution of each sample were determined by mercury intrusion porosimetry in 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.

ϕ_{exp} represents the experimental porosity of the material. ϕ_{disp} is the calculated porosity considering only the dispersed/continuous phases volume ratio. The total porosity of the materials,

ϕ_{total} , can be estimated assuming the complete removal of all the nonpolymerizable components of the emulsion (dispersed phase, water, and surfactant) and in the absence of any shrinking of the monolith during the washing and drying steps. In this work, ϕ_{total} and ϕ_{disp} were calculated with the assumption that all the constituents of the emulsion had a density equal to that of water. Thus, $\phi_{\text{disp}} = 55\%$, and considering that the black liquor contains about 55 wt % of water, ϕ_{total} could be estimated to about 75% for all samples.

Skeletal Density. The skeletal density ρ_s of the materials was determined using a Micromeritics Accupyc 1330 helium pycnometer. An average value of $\rho_s = 1.55 \pm 0.05$ g cm⁻³ was found for all samples prepared.

Specific Surface Area Determination. The specific surface area was determined by N₂ sorption measurements on a Micromeritics ASAP 2010 analyzer. The collected data were subjected to the Brunauer, Emmett, and Teller (BET) treatment.⁵¹

Electron Microscopy Investigations. 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 $\times 500$ and $\times 10,000$. Pieces of polyHIPEs (section of about 0.5 cm²) cut from the corresponding monoliths were mounted on a carbon tab, which ensured a good conductivity. A thin layer of gold-palladium was sputtered on the polyHIPE fragment prior to analysis. Two-dimensional (2D) circular cross sections cell diameter was estimated from SEM micrographs after image processing with ImageJ freeware (NIH, USA). Experimental data were obtained by manual measurements of diameters from a population of at least 100 cells. Several methods have been devised to find a simple factor to convert the mean size of such 2D size distribution to the actual 3D mean size of the spheres without a consensus. A standard assumption in the stereology literature⁵² assumes that the distance between the centre of a given sphere and a random plane that intersects it has a uniform distribution on $[-x, x]$, where x is the radius of the sphere. An approximate solution from this entirely theoretical approach leads to the result that the ratio of the mean diameter of a set of spheres (d_{3D}) to that of its 2D intercept (d_{2D}) is: $d_{3D}/d_{2D} = 4/\pi \approx 1.27$, irrespective of the particular distribution of the 3D sizes.⁵³ We will use this correction factor in this work to estimate the mean corrected diameter (d_m).

The mean corrected diameter (d_m) and the uniformity factor (U) were calculated from the following relations: $d_m = \Sigma n_i d_i / \Sigma n_i$, $U = (1/d^*) \times (\Sigma |d^* - d_i| \times n_i d_i^3 / \Sigma n_i d_i^3)$ where n_i is the number of cells of diameter d_i and d^* is the median diameter (the diameter for which the cumulative undersize volume fraction is equal to 0.5).

Mechanical Analysis. Compression tests were carried out by the Pôle Européen de Plasturgie (Oyonnax, France), at room temperature on a Zwick 1455 dynamometer with a loading cell of 200 N. Cylindrical samples (diameter = 8 mm, length = 10 mm) were compressed at constant speed rate (1 mm min⁻¹) on their flat surfaces. Mean values and standard deviations were



Figure 1. Monoliths obtained from castor oil-in-black liquor emulsions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

calculated from the data obtained with five samples of the same composition.

RESULTS AND DISCUSSION

Sample Preparation

Several HIPEs were prepared with different amounts of TritonTM X-405 and Cremophor[®] EL surfactants using a laboratory-made emulsification system (named “Two-Syringes” emulsification device) specially designed for the preparation of concentrated emulsions.^{25,54} The volume fraction of oil inserted in the emulsion (ϕ) was set at 55%. The amount of epichlorohydrin was set at 10 wt % of the black liquor content, a value corresponding to a slight molar excess relative to the total hydroxyl group content of black liquor. The resulting HIPEs were put into PTFE moulds and heated at 60°C for 48 h to achieve crosslinking.

After solvent extraction and drying, brown, cylindrical self-standing monoliths were obtained (Figure 1). The different samples prepared were codified as follows: M is for Monolith, the second letter indicates the nature of the surfactant used: T for TritonTM X-405 and C for Cremophor[®] EL. The last digit indicates the amount of surfactant used (in percent of the continuous phase). For example, MT2 is a monolith prepared with TritonTM X-405 surfactant at a 2 wt % level.

SEM Characterization

The morphology of the obtained polyHIPEs was observed by SEM. Figures 2 and 3 show representative micrographs. In all cases, the materials have an open cellular structure, the porous morphology appearing to be rather homogeneous, whatever the surfactant used. However, monoliths obtained with TritonTM X-405 (Figure 3) seems to have smaller void size than those prepared with Cremophor[®] EL (Figure 2). At high magnification, the walls of the cavities appear to be constituted of agglomerated nodules whose size increases with the amount of Cremophor[®] EL present in the continuous phase [Figure 2(b,d)]. This type of structure, known as cauliflower,⁵⁵ is typical of micro-gel formation taking place during the curing step, when the continuous liquid phase separates into a solid, polymer-rich phase and a liquid aqueous phase acting as porogen.

Porosity Characterization

Mercury intrusion curves (Figure 4) do not evidence any shrinking or packing at low pressure.

Apart from MT8 sample, narrow pore size distributions above 100 nm are generally observed (Figure 5).

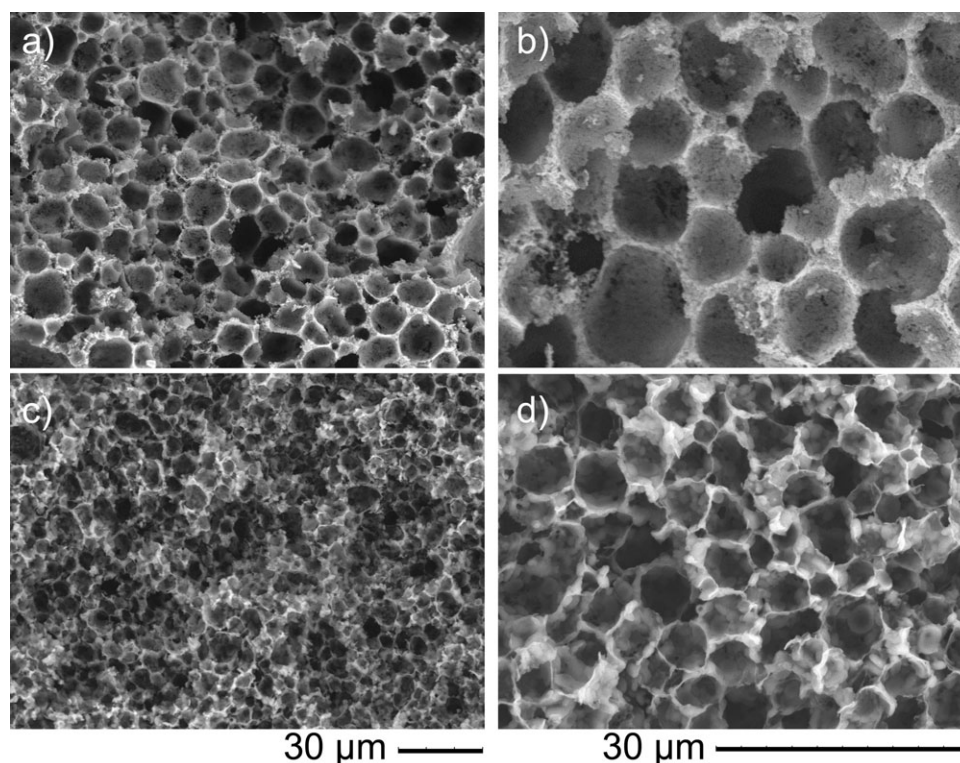


Figure 2. SEM micrographs of MC2 (a,b) and MC8 (c,d) samples.

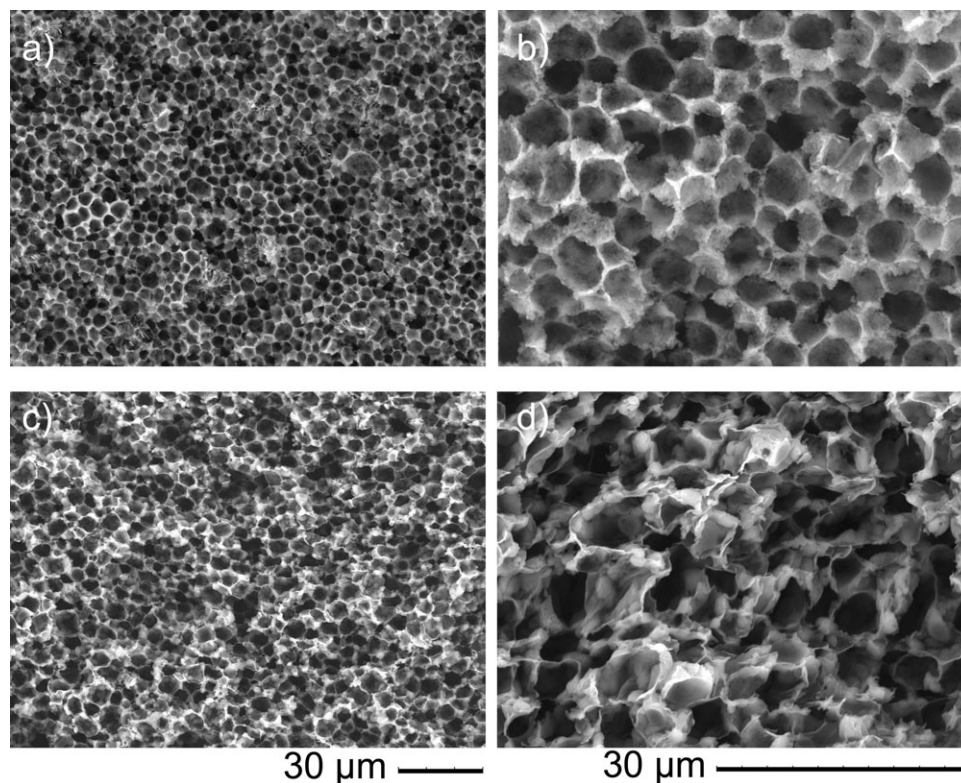


Figure 3. SEM micrographs of MT2 (a,b) and MT8 (c,d) samples .

Porosity characteristics of the different materials obtained are reported in Table 1. The reported neck diameter is the maximum of the pore size distribution of each sample. ϕ_{exp} values are similar for all samples prepared and are closer to the ϕ_{total} values than to the ϕ_{disp} values. This suggests that the water present in the dispersed phase acts as a porogen, leading to the creation of some mesoporosity in the material walls.^{21,22}

Neck diameters around 230 nm are found for samples MT2 to MT6, prepared with Triton™ X-405, MT8 presenting a somewhat larger value. Samples prepared with 4–6% of Cremophor®

EL (MC4 and MC6) show a neck diameter around 1000 nm, whereas for lower and higher surfactant content (MC2 and MC8, respectively) these neck diameters are smaller.

Although a cellular material presenting cells of uniform size (i.e., monodisperse distribution) is susceptible to hold better mechanical and permeability properties than its polydisperse counterpart,⁵⁶ the distribution of the voids size in polyHIPE materials has been barely studied so far. A polydispersity index, U , has been developed for the characterization of emulsions: an emulsion is generally considered as monodisperse when U is smaller than 0.25.⁵⁷ By analogy, we will consider the voids

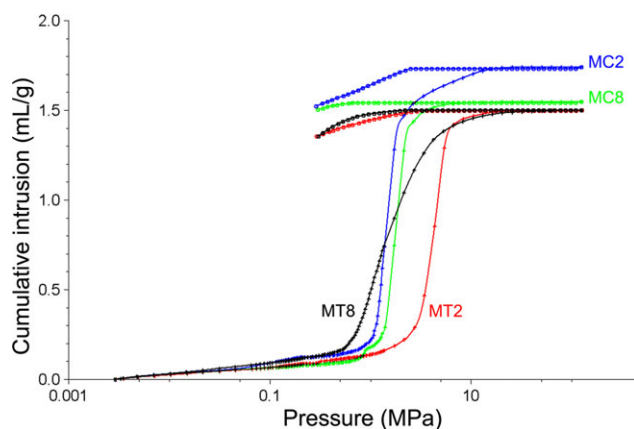


Figure 4. Mercury intrusion curves of MC2, MC8, MT2, and MT8 materials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

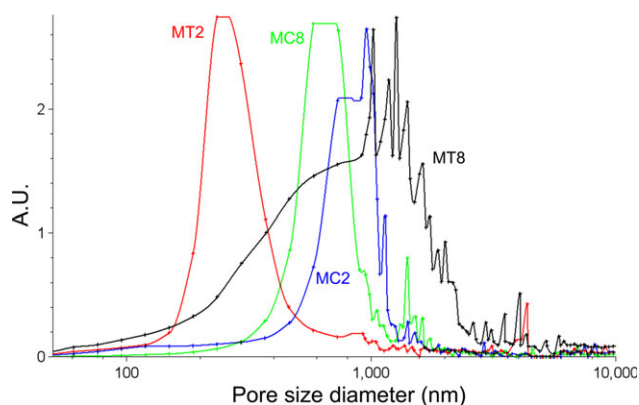


Figure 5. Pore size distribution curves of MC2, MC8, MT2, and MT8 materials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Porosity Characteristics of Black Liquor Monoliths

Sample	MT2	MT4	MT6	MT8	MC2	MC4	MC6	MC8
ϕ_{exp} (%) ^a	71 ± 5	68 ± 3	68 ± 2	71 ± 5	71 ± 4	77 ± 4	78 ± 4	69 ± 4
Neck diameter ^a (nm)	250	180	260	950	850	1100	1200	650
Mean corrected voids diameter d_m (μm) ^b	6	7	6	10	19	16	13	9
U^c	0.3	0.3	0.3	0.9	0.6	0.3	0.3	0.5

^aCalculated from mercury porosimetry data.

^bEstimated from image analysis of SEM micrographs.

^cPolydispersity index, see text for details.

distribution of the monoliths monodisperse under the same conditions. The U value has been calculated for each sample prepared (Table I).

When using low proportions of Triton™ X-405 (MT2 to MT6), the void diameter appeared to be independent of the surfactant amount, and with a rather narrow distribution. More particularly, a 2 wt % fraction of Triton™ X-405 (MT2) was enough to obtain monoliths with a homogeneous void size distribution ($d_m = 6 \mu\text{m}$, $U = 0.3$). In contrast, for the highest amount of Triton™ X-405 tested (MT8), both the mean void diameter and the uniformity factor increased ($d_m = 10 \mu\text{m}$, $U = 0.9$), probably indicating a destabilization of the native emulsion.

Considering Cremophor® EL, mean void diameters are significantly larger than in the case of Triton™ X-405, their value decreasing regularly while increasing the surfactant amount. This behavior can be explained by the fact that an increase in surfactant proportion allows an increased overlapping of the interface, corresponding to the reduction of the droplets size, and thus of the voids. A U value of 0.3, corresponding to a porous morphology very close from monodispersity was obtained for formulations using medium amounts of Cremophor® EL (MC4 and MC6).

Nitrogen sorption analyses showed type IV isotherms characteristic of mesoporous materials for all samples (e.g., MC8,

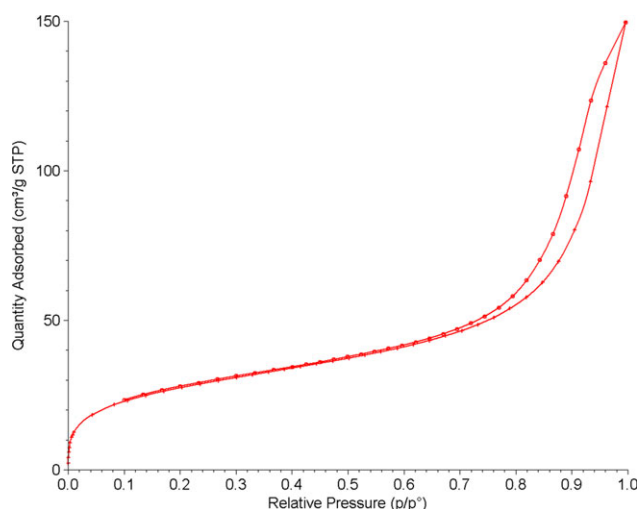


Figure 6. Nitrogen adsorption isotherm of MC8 material. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6). In that case, the BET specific surface area value of $97 \text{ m}^2 \text{ g}^{-1}$ and the calculated average pore size ($\sim 10 \text{ nm}$) agree with the granular structure observed by SEM and with the porogenic behavior of water.^{21,22}

Mechanical Analysis

The compressive Young modulus and the maximal strength values were estimated from the compression stress–strain curves (Figure 7) for MT8 ($E = 27.9 \pm 5.7 \text{ MPa}$; $R_m = 1.8 \pm 0.2 \text{ MPa}$) and MC8 ($E = 16.8 \pm 1.8 \text{ MPa}$; $R_m = 1.0 \pm 0.2 \text{ MPa}$). For comparison, a poly(ethylene glycol dimethacrylate-co-styrene) material with a calculated porosity of 71% and prepared from a 60/40 water-in-oil emulsion showed a Young's modulus of $69 \pm 14 \text{ MPa}$.⁵⁸ Therefore, it can be concluded that lignin-based materials prepared from black liquor, although being less stiff than organic-based monoliths of similar porosity, present rather encouraging mechanical properties.

CONCLUSIONS

Porous materials obtained from castor oil-in-black liquor emulsions reported in this work represent obviously a new example

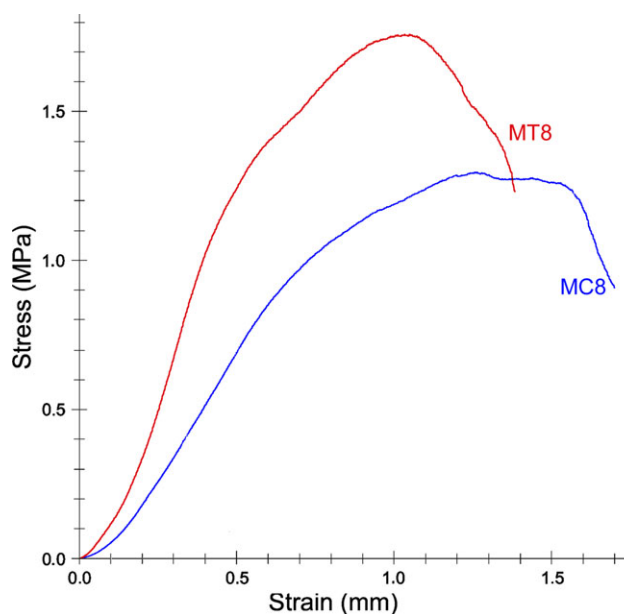


Figure 7. Compression curves of MC8 and MT8 samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of polyMIPE materials as, although being prepared from 55 vol % concentrated emulsions, they possess an interconnected porous morphology. Furthermore, the use of a specially designed emulsification device allows to obtain material with an almost monodisperse void morphology. The nature of the surfactant used has a significant influence on the porous morphology: materials prepared with Cremophor® EL have void diameters about twice larger than materials obtained with Triton™ X-405 have. These monoliths have been prepared from a cheap, easily available renewable biomass raw material using a potentially recyclable vegetable oil as main auxiliary and ethanol as sole extracting solvent. Their preparation is expected to contribute to the polyHIPE materials development.

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