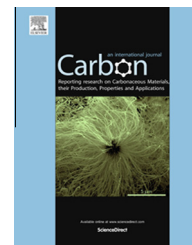


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Lignin-derived macroporous carbon foams prepared by using poly(methyl methacrylate) particles as the template

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ABSTRACT

An efficient route for the synthesis of lignin-derived carbon foams by thermal decomposition of an organic colloid template is described. Lignin, resorcinol, and formaldehyde were reacted by polycondensation into a crosslinked phenolic resin network in the presence of colloidal poly(methyl methacrylate) microspheres as the sacrificial template. Subsequently, carbonization was carried out at 800 °C to fabricate carbon foams with porous structural frameworks. Lignin was used as an excellent candidate for replacing resorcinol or other phenolic substances in the phenolic resin due to its high carbon yield above 50%. The prepared lignin-derived carbon foams had partially open cell structures. The carbon foams had the bulk density and porosity of 0.37–0.60 g/mL and 68.5–82.8%, respectively. Furthermore, the addition of lignin increased the mechanical properties strength of carbon foams.

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1. Introduction

Porous carbon materials have unique properties including monolithic structure, light weight, high specific surface area, high pore volume, and good electrical conductivity [1–5]. These porous carbons have been widely used in a number of fields including thermal insulating materials [6], industrial adsorption and separation processes [2], double-layer capacitors, and capacitive deionization [3,4].

In general, there are two main types of porous carbon materials depending on the origin of the pores: carbon aerogels and carbon foams. Carbon aerogels are prepared by the

sol-gel polycondensation of thermosetting resins such as resorcinol and formaldehyde, supercritical drying, and followed pyrolysis of synthesized organic aerogels [7,8]. On the other hand, carbon foams are fabricated by the carbonization of thermosetting resins, coal, coal tar pitch, and petroleum pitch by removing the volatile matters at high temperature (800–1000 °C) and optional high pressure (2–4 MPa) under inert atmospheres [5,6]. In recent times, synthesis of carbon foams using a template has become an active field of research because well-defined pores, pore sizes, and pore structures are readily controlled when the template is removed [1,2]. Organic templates are particularly beneficial for controlling

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the structure of carbon because they can be dissolved using an appropriate organic solvent or decomposed during carbonization [9–11].

Lignin, the main by-product of pulp and paper industries, is an abundant, cheap, renewable, and nontoxic natural polymer. Lignin is composed of phenyl propane units and has a highly crosslinked structure close to the network of phenolic resin [12,13]. The reactivity of lignin is greater than that of cellulose and other natural polymers and very similar to that of tannin which has the greatest reactivity [14–17]. Also the presence of aliphatic, phenolic, and hydroxylic groups makes it possible to chemically modify lignin for various applications [18]. While cellulose forms linear and partially aggregated crystalline configurations, lignin exists as random and noncrystalline structures that are responsible for its outstanding compressive strength and thermal stability [19]. The phenolic units of lignin can react with formaldehyde to form methylol derivatives that condense internally or with other phenols under alkaline condition [20]. Therefore, because of its structural similarity with phenol, lignin as well as tannin are promising natural alternatives to synthetic phenol in the fabrication of phenolic resins, and the obtained product is cheaper and less toxic. Thus, lignin is advantageous in terms of both economic and environmental points of view [13,21].

Herein, we report on the synthesis of carbon foams from an integrated crosslinked network of lignin (L)-resorcinol (R)-formaldehyde (F) in the presence of poly(methyl methacrylate) (PMMA) particles as the pore generator, followed by carbonization. The effect of the amount of lignin and PMMA colloidal particles on intrinsic characteristics of carbon foams such as the morphology, carbon foam structure, and physical properties such as thermal property, compressive strength, and electrical conductivity were investigated.

2. Experimental

2.1. Materials

Resorcinol and formaldehyde solution (35–38%) were supplied by Junsei Chemical Co. Ltd. (Japan), and lignin was purchased from Sigma Aldrich (USA). Sodium hydroxide was purchased from Daejung Chemicals Co. Ltd., (South Korea) and PMMA particles, SUNPMMA-S50 (average diameter: 6.4 μm), were provided by Sunjin Chemical Co. Ltd., (South Korea). Acetic acid (99.5%) and methanol (99.9%) were obtained from OCI Chemical Ltd. (South Korea) and Duksan Pure Chemical Co.

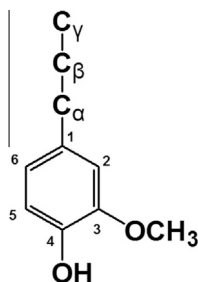


Fig. 1 – Generalized chemical structure of lignin.

Ltd. (South Korea), respectively. All solutions were prepared from deionized and distilled water.

2.2. Preparation of precursor solutions and carbon foams

An LRF precursor solution was prepared to control the precursor molar ratio (1:2) for L + R and F, respectively, and a total of 30 wt.% organic content (L + R + F mass). Resorcinol was replaced by kraft lignin on a weight basis. A generalized chemical structure of lignin is given in Fig. 1. The molecular weight of the phenyl propane unit (C₉) in kraft lignin was considered to be approximately 190, and the reactive site per C₉ for methylation was assumed to be 0.4 [13,22]. Sodium hydroxide (C) was used as a base catalyst and the LR/C ratio was 50. Subsequently, PMMA particles were added as a template into the reaction system and the reaction mixture was magnetically stirred until the PMMA was mixed completely. The resulting homogeneous LRF-PMMA mixtures were cured at room temperature for 24 h.

Next, the LRF-PMMA resins with dilute acetic acid (10 wt.% solution in water) were placed in an oven at 85 °C. This aging step was employed to increase the mechanical properties of the resins by crosslinking reactions of methylene ether bonds to establish bridging networks between neighboring phenyl groups [7,23]. Then, they were soaked in methanol to exchange residual water [11]. Upon completion of the aging and drying cycles, the LRF-PMMA resins were carbonized in a tube furnace under argon atmosphere from room temperature to 400 °C at a rate of 1.5 °C/min for 4.5 h, held at 400 °C for 1 h to completely eliminate PMMA particles, to 800 °C at a rate of 1.5 °C/min for 4.5 h, and then held at 800 °C for 3 h to pyrolyze the LRF-PMMA resins. During the carbonization step, LRF-PMMA resins were transformed into porous carbon structures by thermal decomposition of PMMA templates and other molecules. Finally, the furnace was cooled down to room temperature under argon atmosphere, and the carbon foams were obtained as black rigid monoliths. Throughout this paper, carbonized products are designated on the basis of the LRF-PMMA mixture content. For example, P200L60 was prepared by blending 60 wt.% lignin in lignin and resorcinol and 200 wt.% PMMA to lignin, resorcinol and formaldehyde.

2.3. Characterization

The morphologies and structures of the LRF-PMMA resins and carbon foams were analyzed using a Hitachi S-4300 field-emission scanning electron microscopy (FE-SEM) at an accelerating voltage of 15 kV. The structure of the carbon foams was examined using Rigaku D/max-2200. X-ray diffraction (XRD) patterns obtained by employing the Cu K α irradiation ($\lambda = 0.1541 \text{ nm}$) at 40 kV. Shrinkage of the LRF-PMMA resins and carbon foams was calculated from dimensional measurements using an electronic Vernier caliper. Bulk density of the carbon foams was calculated as the average value of mass divided by volume. Skeletal density was measured by Accupyc II 1330 helium pycnometer (Micromeritics) using finely crushed samples for avoiding any erroneous results related to possibly closed porosity. Porosity of carbon foams is calculated from bulk and skeletal density. The decomposition

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