SYNTHESIS AND CHARACTERIZATION OF CARBON FOAM DERIVED FROM CONTROLLED FRACTIONS OF KRAFT LIGNIN

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ABSTRACT

Here, we report an efficient route for the synthesis of resin-derived carbon foams (CF) with controlled lignin-phenol-formaldehyde fractions by thermal decomposition of a sacrificial mold. The lignin employed were kraft lignin (LK), ethyl acetate insoluble LK fraction (LFIns) and ethyl acetate soluble LK fraction (LFSol). The gradual development of the carbon nanostructure in the CFs was studied using the complementary methods of Raman spectroscopy and XRD. In the Raman spectra, the D and G bands, typical features of carbonaceous materials, centered at approximately 1320-1360 cm^{-1} and 1580-1600 cm^{-1}, respectively, were identified. It was observed that the I_D/I_G ratio increases for the CF produced with the KL and LFIns fractions indicating the increase in the proportion of condensed aromatic ring structures with defects. The decrease in the I_D/I_G ratio for the Control and LFSol samples is directly related to the increase in crystallinity. Two broad peaks at 2θ diffraction, around 22.9° and 43.9°, were detected for all samples and were attributed to reflections from the Miller crystallographic planes (002) and (100) of amorphous carbon. It was possible to observe the decrease in intensity of these peaks in the KL and LFIns samples, which indicates a low degree of graphitization of the carbon. Micrographs showed that the carbon foams had macropores (cells) surrounded by carbon walls (ligaments) and most of the cells were connected through holes (windows) formed in the carbon wall. Noting that the voids left by the sacrificial mold (PU) created the cellular structure of the carbon foam derived from skeletons in polyfaceted or spherical integral cells. It is expected that the synthesized carbon foams can be applied in current areas focused on functional materials that require better thermal and conductive properties at the same time.

Keywords: *Carbon foam; kraft lignin; Carbonization; nanostructure.*

INTRODUCTION

Recently, the production of Carbon Foams (CF) using precursors from renewable sources has been greatly investigated, in view of the demand for technologies that allow the reduction of the emission of pollutants responsible for climate change, along with the volatile prices of oil and conventional polyurethane.(INAGAKI; QIU; GUO, 2015) According to the literature, CF are called functional materials, due to their inherent properties, such as: excellent thermal and electrical conduction, electromagnetic shielding, good water repellency and efficient oil adsorption (INAGAKI; QIU; GUO, 2015; QU et al., 2017).

There are several methodologies for the fabrication of carbon foam, such as: carbonization of polymer precursors; Blowing of carbon precursors; Compression of exfoliated graphite; Assembly of graphene nanosheets and among others.(INAGAKI; QIU; GUO, 2015) Among these approaches, the direct carbonization of a sacrificial mold and the use of polymeric precursors as a carbon source is the most used and low-cost method. Phenolic resin is one of the most popular polymer precursors due to its high carbonization capacity.(INAGAKI et al., 2014) Usually, phenolic resin is made from the polymerization between phenol and formaldehyde. The studies employing lignin-phenol-formaldehyde resin (LPF) as a carbon source in the synthesis of CF discusses extensively the difference in calcination temperature, but do not take into account the difference in molar mass employed between the different lignin fractions.(INAGAKI; QIU; GUO, 2015; QU et al., 2017; YAN et al., 2021)

Thus, the present work is a continuation of the work presented previously by Rodrigues *et al.*, here we will analyze the structure-property correlation of CF produced by different fractions of KL. Here, we report for the first time the synthesis of CF from fractions of kraft lignin (KL), as carbon source, and polyurethane (PU) foam, as sacrificial mold. The different lignin fractions employed on the intrinsic characteristics of CF, such as the morphology, nanostructure, and physical properties, such as the thermal and electrical property were investigated. The results indicated that the foam synthesized with fraction of KL soluble in ethyl acetate (FLSol) had very similar properties to the control resin with 100% phenol.

MATERIALS AND METHODS

The carbon precursor resin was synthesized according to the methodology discussed in our previous paper. Initially, KL from *Eucalyptus urograndis* wood was refined by a sequential fractionation process in ethyl acetate (EtAc). And then employed in partial phenol replacement in the synthesis of LPF resin. The lignin employed in this study are the unprocessed KL, the insoluble fraction of KL in EtAc (LFIns) and the soluble fraction of KL in EtAc (LFSol). The carbon foams were prepared using PU foam, as sacrificial mold, and the resins prepared in section 2.2, as the carbon source. In a typical synthetic procedure, the resin was poured onto the PU foam mold with a size of 2.4 x 1.2 x 1.0 cm^3, length, height, and width, respectively. Air bubbles inside the PU foam scaffolds were removed by frequently squeezing the scaffolds with a glass rod during the infusion of the solution.23 The PU foam treated with KL resin was then placed in an oven at 80 °C for 12 h for complete solvent evaporation and polymerization. Carbonization of the PU/KL composite was carried out in a tube furnace under nitrogen atmosphere. The PU/KL was heated from room temperature to 1000 °C at a rate of 5 °C.min-1, held at 1000 °C for 2 h and then cooled naturally to room temperature.26 Finally, the carbon foam was obtained and named according to the nomenclature used by the resins. Similar procedure as described was employed for the synthesis of the other CF.

Structural properties

The crystal structures of the CF were investigated by powder X-ray diffractometry in the XPert Pro MPD equipment, from PANalytical, using Cu Kα radiation, operated with a voltage of 40 kV and current of 40 mA. Diffractograms were collected in a continuous mode within a 2θ value range from 5° to 60° per θ/2θ scan configuration. XRD analyses were performed at the RawMatters Research (RAMI) department of the School of Chemical Engineering at Aalto University (Espoo-Finland). The nanostructure of the carbon materials was in addition analysed with a Renishaw inVia™ Confocal Raman Microscope using a laser at 532 nm. Before the analysis, the instrument was calibrated using a silicone reference sample. The Raman spectra were acquired using a 20x objective lens and a 30 s laser exposure time. The spectra were collected between 800 and 2000 cm^{-1}. At full laser power, we noticed severe surface damages and significant nanostructural changes caused by overheating of the sample. We needed to adjust the laser power to 30 mW of the 40 mW maximum output power to minimize the laser-induced overheating as preconized in Beyssac *et al.*[27]. Five spectra were taken from each sample at different locations. The spectra were smoothed, and background corrected using the Renishaw WiRE 5.3 software.

Textural properties

The morphological characterization of the CF was performed by Scanning Electron Microscopy (SEM), Zeiss model Sigma VP, with an applied acceleration voltage of 5 kV. The samples were sputter-coated with gold to ensure electric conductivity (20 mA current with 90 s coating time). To determine the diameter of the macropores, about 100 pores in the SEM micrographs of each specimen were analyzed by ImageJ software.

RESULTS AND DISCUSSION

Nanostructural evolution

The gradual development of carbon nanostructure in CF was studied using the complementary methods of Raman and XRD spectroscopy, Figure 1. As Raman spectroscopy is particularly sensitive to sp^2 carbon structures and their characteristics are measured at the nanometer scale, it has become a technique widely used to assess the development of microstructures in carbon-based materials.(GUIZANI et al., 2017; SMITH et al., 2016) The Raman spectra of the Control, KL, LFSol and LFIns carbon foams were shown in Figure 1A. D and G bands, typical features of carbonaceous materials, were identified in the spectrum of the samples, centered at approximately 1320-1360 cm^{-1} and 1580-1600 cm^{-1}, respectively. In general, the D band is associated with disorder and defects present in the sp^2 graphitic carbon structure, i.e., point defects such as vacancies and dopant atoms. On the other hand, the G-band is related to the in-plane vibration of sp^2 hybridized carbon structures, characteristic of highly ordered regions of graphite crystals.(SMITH et al., 2016) Thus, both the D-band and G-band indicated carbon nanocrystallites with sp^2-turbostatic nanostructure with small crystals and random ordering, mainly due to the non-graphitizable nature of the precursor lignin and the high carbonization temperature (UDAYAKUMAR et al., 2021).

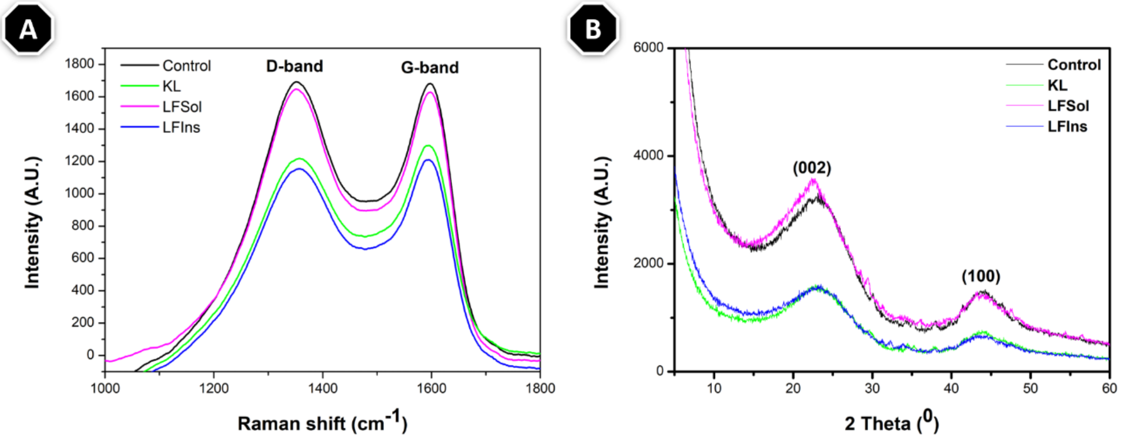

Figure 1: (A) Raman spectrum and (B) X-ray diffraction analysis for carbon foams synthesized with different lignin fractions: KL, LFSol and LFIns.

The I_D/I_G ratio increases for CF produced with the KL and LFIns fractions, indicating an increase in the proportion of defected condensed aromatic ring structures. The decrease in the I_D/I_G ratio for the Control and LFSol samples is directly related to the increase in local order.(ROIS et al., 2021; SETO et al., 2021) The I_D/I_G range between 0.97-0.99 was related to aromatization of the lignin structure, through condensation of smaller aromatic rings into larger aromatic structures as a result of the high temperature treatment.(ROIS et al., 2021) The same can be observed for the FWHM ratios of the D and G bands of the samples, which indicated a higher degree of order with decreasing values.(ESCRIBANO et al., 2001)

X-ray diffraction (XRD) is a complementary technique to Raman spectroscopy that allows analyzing the crystalline structure of a material (Figure 1B). Two broad peaks at 2θ diffraction, around 22.9° and 43.9°, were detected for all samples and graphite distributed to reflections from the Miller crystallographic planes (002) and (100) graphitic carbon and graphite lattice planes, respectively. These results imply that all carbon particles had amorphous porous structures and were partially graphitized through the simple carbonization process, although complete graphitization requires much higher temperatures (2600–3300 °C).(CAO et al., 2021) It was possible to observe the decrease in the intensity of these peaks in the KL and LFIns samples, which indicates a low degree of carbon graphitization.

Textural analysis

The SEM micrographs of the CF cross section produced with different lignin fractions from LPF resin were shown in Figure 2. The micrographs showed that the CF had macropores (cells) surrounded by carbon walls (ligaments) and most of the cells were connected through holes (windows) formed in the carbon wall.(YAN et al., 2021) Noting that the voids left by the sacrificial mold (PU) created the cellular structure of the CF, derived from skeleton-struts to integral poly-faced or spherical cells.(INAGAKI; QIU; GUO, 2015)

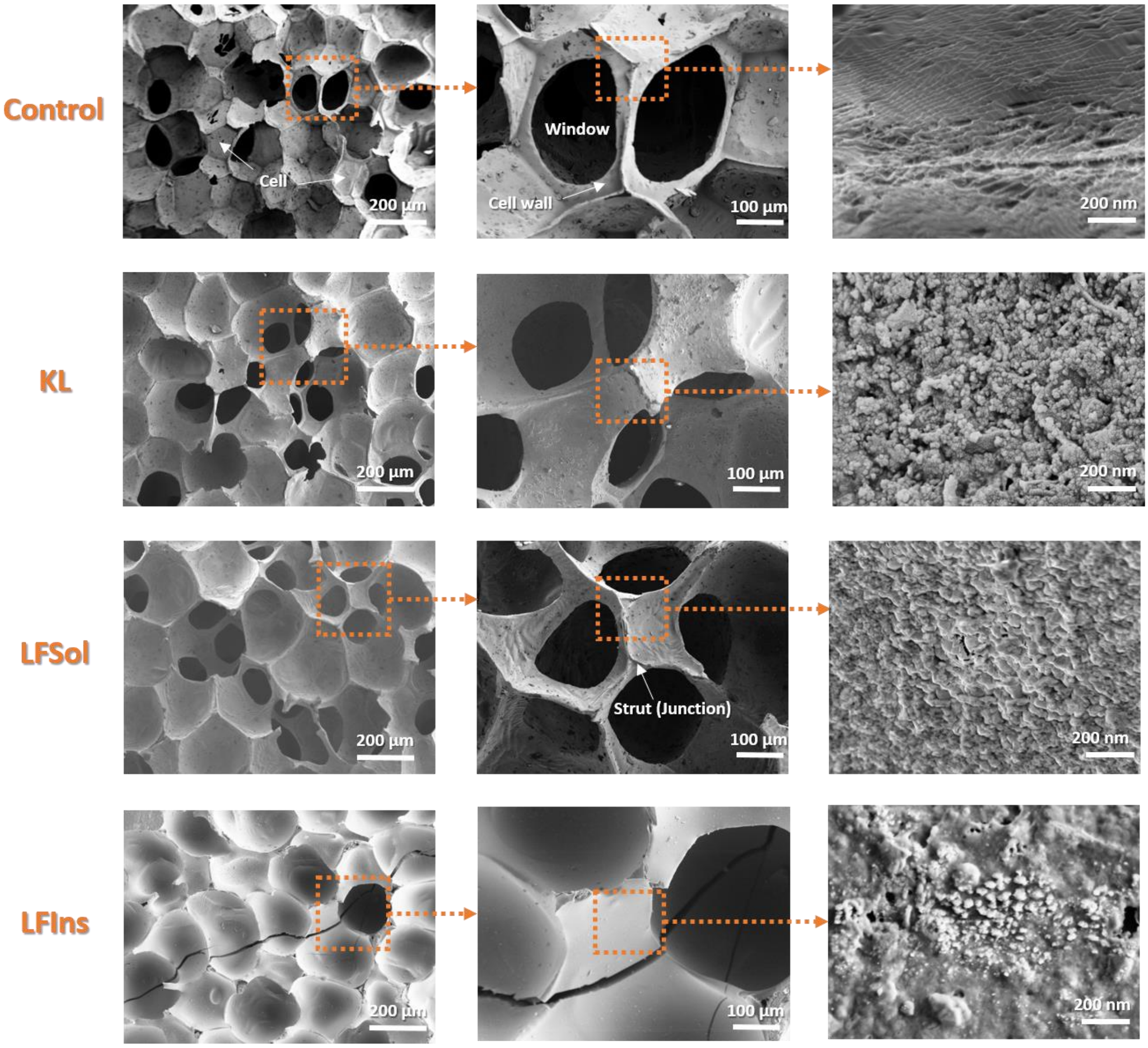

Figure 2: SEM micrographs of the cross section of different carbon foams.

The use of a template allowed greater control over the macropore structure of the material, making it possible to obtain windows with equivalent dimensions and cells evenly distributed over the surface of the CF. To determine the diameter of the macropores, about 100 pores in the SEM micrographs of each specimen were analyzed by ImageJ software. After a systematic evaluation of pore size in the macropore range, CF exhibited a porous surface with narrow ligaments and average macropore diameter around 280-420 µm, whose average porosity ranged from 68-80%, indicating that it is a promising absorbent material. However, the SEM images of the LFIns sample clearly showed the presence of cracks in the cell walls, low window content and increase in average macropore diameter. Such an event may be linked to the fact that the contaminants (Na and S) and particulates present in FLIns affected the cell nucleation process in the preparation of CF. The existence of contaminants and particulates in FLIns was widely discussed in our previous work. Thus, the resin derived from FLIns impregnated heterogeneously in the sacrificial mold and in regions with an excess of these impurities, brittle regions were formed. And when carbonized, a region of instability was generated, causing the pores to have a more dilated appearance, which could be the junction of two or more pores, and cracked.

CONCLUSIONS

The results indicated that the foam synthesized with fraction of KL soluble in ethyl acetate (FLSol) had very similar properties to the control resin with 100% phenol. CF produced with the KL and LFIns fractions indicating the increase in the proportion of condensed aromatic ring structures with defects. The decrease in the I_D/I_G ratio for the Control and LFSol samples is directly related to the increase in crystallinity. It was possible to observe the decrease in Raman intensity of these peaks in the KL and LFIns samples, which indicates a low degree of graphitization of the carbon. Micrographs showed that the carbon foams had macropores (cells) surrounded by carbon walls (ligaments) and most of the cells were connected through holes (windows) formed in the carbon wall. Noting that the voids left by the sacrificial mold (PU) created the cellular structure of the carbon foam derived from skeletons in polyfaceted or spherical integral cells. SEM images of the LFIns sample clearly showed the presence of cracks in the cell walls, low window content and increase in average macropore diameter

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