LIGNIN/COLLAGEN HYBRID BIOMATERIALS AS BINDER SUBSTITUTE FOR SPECIALTY GRAPHITES AND ELECTRODES

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ABSTRACT

Sustainable biomaterial binders were developed from lignin and collagen to replace the conventional petroleum pitch and coal tar pitch binders that have been used when making specialty graphites and graphite electrodes. The team prepared lab-scale graphite electrodes by first creating green composites, by hot-pressing together the lignin, collagen, petroleum coke, and other additives, followed by carbonization and graphitization. Response Surface Methodology (RSM) experimental design was employed, based on Box-Behnken Design (BBD). This was employed to optimize the recipes and processing protocols for the green composite hot-

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pressing of 3.5 cm diameter $\times$ 19 cm long cylinder specimens. Relative to density, the apparent optimum conditions occurred with 13.0% lignin, 3.6% collagen, 27.4% petroleum coke fines, and the balance of petroleum coke particles plus some additives. The green hot-pressing protocol employed 30 MPa pressure at 400 °C for 2 hours. Baking peaked at 800 °C, ramped up and down over 13 days. This baked product hosted an apparent density of 1.67 g/mL, and exhibited 6.2% puffing. Another baked product hosted 1.56 g/mL and 1.67% puffing. After the baked product was graphitized, we achieved an apparent density of 1.51 g/mL and resistance of 25-30 $\mu\Omega\text{m}$. These results approached the specifications for specialty graphites.

1. Introduction

Pitches, either derived from petroleum or from coal tar pitches, have been conventionally used as the binders when preparing graphitized products from petroleum cokes. The graphitized products have included carbon anodes, electric motor brushes, and graphite electrodes. However, when petroleum pitches and coal tar pitches are carbonized, the reactant dehydrogenation polymerization, aromatization and rearrangement process [1] can release volatiles that may cause cancer at high doses. These can include polycyclic aromatic hydrocarbons (PAHs) in the range of 3-7 rings, and heterocyclic compounds [2-3]. Moreover, these pitches are comprised of PAHs; and the European REACH regulations are imposing strict protocols for transporting and processing PAHs. Lignin and collagen, in their raw form, are not construed as PAHs. Due to the restrictive legislation concerning the use of PAHs and the emission of these pollutants, and the sharp decline in coal tar supply, several attempts have aimed at finding a suitable substitute for these pitches, including pitch blends [4], organic resins [5], bio-oil residue [6], etc. Also there is great interest in developing novel uses for biomass and its derivatives that can offer sustainable alternatives to mined petroleum-based materials. However, one crucial question that has to be

asked when assessing feedstock is which binders are capable to assume the role of petroleum pitch or coal tar pitch in carbonaceous products manufacturing. Specifically, what biomass source can offer a high coke yield [7], cross-linking polycyclic aromatic hydrocarbons [4], and a high atomic C/H ratio, etc [8]. Clean lignin poses the opportunity for achieving these properties.

The Penn State team has been collaborating with Furness-Newbuge to develop novel environmentally-friendly bio-binders from lignin plus collagen plus other additives during the past few years. Lignin, the second most abundant naturally occurring aromatic polymer, has been traditionally relegated to use as a low-grade fuel, or under-utilized byproduct from pulping and ethanol production processes. However, its structure and behavior lends itself as a novel candidate for specialty high-temperature adhesives and carbonized materials manufacturing [9-10]. Similar to the liquid phase carbonization of coal tar pitch, lignin pyrolyzes via a free-radical chain-reaction mechanism [11]. The cleavage of its alkyl-aryl ether linkages and free end groups, can generate multiple free-radicals when lignin experiences heat treatment [12]. These free-radical precursors sequentially undergo a variety of thermally induced reactions, including crosslinking, aromatization, and rearrangement reactions, which lead to the formation of highly-condensed aromatic rings [13-14]. These condensed rings ultimately develop into heterogeneous carbon structures of a highly graphitic nature [15-16]. As this transformation occurs, the electrical resistivity of these lignin chars decreases significantly with the increase of carbonization temperature; and the graphitized product can exhibit outstanding electro-conductivity [17]. Moreover, probably due to the highly cross-linked and refractory nature of the lignin chars, these materials release fewer PAH volatiles, when compared to chars from other biomass constituents, such as chlorogenic acid, pectin, cellulose and tobacco [18].

Collagen represents a biomass feedstock derived from the hides and residues from the meat-packing industry. The signature characteristic of collagen is its triple helical structure intertwined in three repeating tripeptide chains. This particular structure normally becomes unstable by irreversible hydrolytic denaturation, resulting in helix-to-coil transition and conversion into water-soluble gelatin [19]. Owing to the ampholytic behavior with ionizable groups and abundant active sites for crosslinking reactions, collagen serves as a strong binder. Collagen-derived gelatin also possesses superior advantages for the fabrication of electrodes, such as high-strength bonding properties, effective dispersion ability for raw materials, and excellent electrochemical stability [20-21].

Previous Penn State work has discerned that collagen plus other additives could successfully serve as a core binder, when casting iron in foundries [22-25]. Even at somewhat-elevated temperatures, collagen possesses favorable physical and mechanical properties; and it also releases far less volatile organic compound (VOC_{C6-C16}), hazardous air pollutants (HAP) and greenhouse gas emissions than do conventional phenolic urethane-based binders [22-25]. As a further application, when the Penn State-Furness Newburge Team used lignin, collagen and other additives to bind together anthracite fines into bricks, these bricks offered a favorable fuel source in foundry cupolas, as a replacement for conventional coke. The bindered anthracite bricks exhibited superior unconfined compressive (UC) strength in all the thermal stages that are encountered in the cupola furnace [26, 27]. Specifically, collagen maintained its structural integrity through hydrogen bonds at ambient temperature, while the lignin-collagen hybrid system underwent a series of fusing reactions in-situ that even imparted the strength that kept the bricks in-tact up to 1400 °C in the heat zone of a full scale cupola [26, 27]. Based on these favorable results with core binders and bindered anthracite bricks, the authors herein next set out

to explore whether these benign biomaterial-based binders from lignin and collagen could replace petrochemical pitches for the fabrication of graphite electrodes.

In **recently published** work by the Penn State team [28], the authors offered thermogravimetric concurrence and insight to the thermal-binding synergism between lignin and collagen, and revealed that considerable pyrolytic gaseous products released at the temperature range of 150-500 °C when the lignin was blended with collagen.

The objectives of the research herein have been to (a) devise lignin-collagen based binders that could replace coal tar pitches or petroleum pitches when preparing the precursors for specialty graphites; and (b) move in a favorable direction by optimizing (i.e. increasing) the apparent density of the baked product, and decreasing its puffing. Specifically, by analyzing the performance parameters of baked products, the research team iteratively adjusted the baking program to achieve a more favorable product, as guided by utilizing the response surface methodology (RSM) of the Box-Behnken Design (BBD).

By this process, the authors evaluated how an array of independent variables influenced the apparent density of the baked product. Many of these parameters pertained to preparing optimal conditions to prepare the green composites by the hot-pressing technology. The independent variables mentioned above were prescreened by fractional factorial experiments and single factor experiments. In order to improve the physical and mechanical properties and enhance the structural integrity of the resulting products, the authors also monitored the occurrence and development of puffing during the baking process. Also, the team employed analytical techniques such as scanning electron microscopy (SEM), optical microscopy, **and (occasional)**

Raman spectroscopy so as to monitor the morphology changes in the bio-binder and petroleum coke system under various conditions.

The authors herein have employed Raman spectroscopy to provide guidance relative to extent to which these products became graphitized and ordered. Zickler et al. [29] appraised pyrolyzed wood over a broad range of temperature from 400 to 2400 °C, and observed that with increasing temperature, the Raman area ratios I-D-band / I-G-band progressively increased with temperature up to about 900 °C, and then generally decreased above that temperature, up to 2400 °C. In comparison, when using x-ray diffraction, Zickler et al. [29] observed that the crystallite characteristic size L_a progressively increased with increasing temperature, reaching its highest level at 2400 °C.

2. Experimental

2.1. Materials

Clean lignin was obtained from Domtar of South Carolina, USA. This lignin had been extracted from pine softwood pulping operations, and then desulfurized by a lignin cleaning and desulfurization process. Prior to use, lignin was pre-dried at 50 °C for 72 h and then ground into fines less than US # 100 mesh. Collagen, derived from an animal tissue source by an aqueous extraction process, was received as granules from Entelechy (Plymouth, MI). Petroleum coke was provided by SGL Group of Morganton, NC, and was used in the form of particles or fines. Sieve analysis for petroleum coke particles and fines are listed in Table 1. The main characteristics of these raw materials are tabulated in Table 2. The lignin hosted 65% carbon by weight and 0.06% nitrogen, and about 27% oxygen; whereas collagen contained 47% carbon, 17% nitrogen, and 27% oxygen. The petroleum coke contained 98.4% carbon, 0.8% nitrogen,

and 0.05% oxygen. These components, along with other additives, were blended together prior to fabrication. The proportions are listed as the percent of all petroleum coke that was fines (i.e. % fines + % particles = 100%). Then also the percent of the total dry mass that was lignin or collagen.

Table 1 - Petroleum coke sieve analysis (mass basis, %).

Sieve diameter (mesh)	14 - 20	20 - 30	30 - 40	40 - 50	50 - 100	100 - 200	< 200
Petroleum coke particles (%)	8.33	61.29	25.18	4.40	0.46	0.10	0.24
Petroleum coke fines (%)	—	—	—	—	7.39	53.49	39.12

Table 2 - Main characteristics of raw materials (dry basis, Wt.%).

Sample	Ultimate analysis					Proximate analysis		
	C	H	N	S	O*	Volatile matter	Fixed carbon	Ash
Lignin	65.11	6.04	0.06	1.77	27.02	80.26	18.65	1.09
Collagen	47.32	7.25	17.35	0.93	27.15	95.65	3.85	0.50
Petroleum coke	98.38	0.15	0.82	0.60	0.05	8.88	91.02	0.10

* oxygen computed by difference.

2.2. Green Composite Preparation by Hot-Pressing

Prior to fabrication, the collagen was dissolved into a small amount of water (30 mL H₂O / 200 g dry constituents, typically) at 70 °C to form a solution gel. After mixing the petroleum coke with the lignin, these two were added into the collagen solution, and the blend was stirred until all the ingredients were thoroughly homogenized. The blended mixture was next compacted into a cylindrical mold (3.5 cm diameter, 19 cm height) that had been pre-coated with dry film lubrication. Next, the mold and its contents were compacted at a prescribed temperature (100 to 400 °C) in an airtight hot-pressing system (see Fig. S1 in Support Information). The upper temperature bound of the hot-pressing system was 400 °C. Ultra-high purity nitrogen was purged

through the hot-pressing enclosure, so as to remove all the intermediate gaseous products. Under these constant conditions, the mixture was thermally pressed from both ends for the selected soaking time of 1 to 4 hours, at 30 to 75 MPa pressure, so as to obtain a high-density. The resulting product, known as the **hot-pressed** green composite (see Fig. 1a), was taken out of the mold, and allowed to cool down to ambient temperature. The green composite dimensions were 3.5 cm diameters by 9 to 12.5 cm long.

Fig. 1 - Different types of carbon products: (a) green composite; (b) baked product; (c) graphite electrode.

2.3. Baked Product

Next, the baked product was prepared by baking the green composites at 800 °C under pure nitrogen for prolonged durations of 52 to 480 hours. This baking protocol was carried out in either a horizontal or vertical tube furnace, wherein the carbonization of the baking samples was achieved within a quartz tube enclosure. Ultra-high purity nitrogen with a flow rate of 50 mL/min was used as an inert atmosphere to prevent oxidation during heating, baking and cooling. For these tests, an array of baking programs was employed, as illustrated in Fig. 2. These programs appraised the effect of the baking rate and cooling rate on the properties of the baked

products (see Fig. 1b). Amongst these, Protocol C offered the more favorable outcome (see Results), and was used in all subsequent experiments unless otherwise specified.

Fig. 2 - Baking programs for test electrodes: (A) baking rate of 0.25 °C/min to 500 °C, then 1.25 °C/min to 500 to 800°C, cooling rate of 1.08 °C/min; (B) baking rate of 0.10 °C/min to 500 °C, then 0.21 °C/min to 500 to 800°C, cooling rate of 1.08 °C/min; (C) baking rate of 0.04 °C/min to 500 °C, then 0.07 °C/min to 500 to 800°C, cooling rate of 1.08 °C/min; (D) baking rate of 0.04 °C/min to 500 °C, then 0.07 °C/min to 500 to 800°C, cooling rate of 0.07 °C/min.

2.4. Graphitization Treatment

In order to yield graphitized electrodes (see Fig. 1c), some of the more favorable baked products were forwarded to SGL Carbon Co. Ltd. in Monmouth NC. There, SGL employees placed these samples on top of full-scale graphite electrodes, and then graphitized the samples

concurrently with the full-scale electrodes at 2800-3000 °C for several weeks per their standard protocol.

2.5. Apparent Density, Puffing, and Electrical Resistivity Test

Apparent density was determined by the use of Archimedes' principle and used a protocol including weighing a specimen in air (W_a), and in water (W_w). Specifically, the cylinder samples were hung from the balance by a wire, and then submerged in water. Apparent density was discerned by $[W_a \times \rho_{\text{water}} / (W_a - W_w)]$, where ρ_{water} is the density of water. The mass in water was measured with 5 seconds of submergence. The surfaces of these products were rather smooth, and we observed scant air bubbles affixed to the surface of the sample. The exception to this was that we did observe air in cracks, but perceived this as true-reflection of the character of these specimens. With time, as air escaped from these cracks, the measured apparent density went up, but the values reported herein reflect the mass as monitored within 5 seconds of submergence.

Puffing was defined as the maximum linear expansion of the specimen after baking, computed as $[(\text{final length} - \text{initial length}) / (\text{initial length})] \times 100\%$. The authors also semi-qualitatively monitored the extent of horizontal and vertical cracking in the cylinder samples.

For baked products, electrical resistivity was measured by using an Agilent HP-4980 LCR meter and a solid dielectric test fixture wrapped with the brass film on each end. Before each test, each face of the baked product specimen was ground and polished with abrasive to ensure comprehensively close contact between the specimen and brass films. After a short compensation of the solid dielectric test fixture, the resistance (R , $\mu\Omega$) was obtained at the condition of 100 mV input power and 20 Hz frequency. The electrical resistivity (ρ , $\mu\Omega\text{m}$) was

calculated from the formula as follows: $\rho = RA / L$, where A (m²) is the contact area between the specimen and the solid dielectric test fixture; L (m) is the specimen length. The results listed herein depict the averages of four replicate analyses.

For the graphitized specimens, electrical conductivity was measured by SGL employees who used SGL's standard protocol. This was similar to that described above.

2.6. Raman Spectroscopy

Raman spectroscopy employed a WITec CRM 200 confocal MicroRaman system, with cooled CCD camera and 488nm, 515 nm, 633nm, and 785 nm laser lines. The protocol employed a 40X microscope objective to focus the excitation laser beam and collect the Raman scattering signal.

2.7. Response Surface Methodology

Response Surface Methodology (RSM), coupled with Design-Expert® software (Version 9, Stat-Ease, Inc., Minneapolis, MN) has provided a time-saving and efficient way for researchers of multi-variable systems to devise experimental designs, response surface regressions, statistical analysis and process optimizations. A standard RSM design called Box-Behnken Design (BBD) was chosen in this study to fit the second-order polynomial models and to determine the optimal conditions for the independent variables. The independent variables and their experimental ranges investigated herein were preliminarily determined by the fractional factorial experiments and single factor experiments. The adequacy of the fit of the polynomial model was evaluated by multiple criteria derived from analysis of variance (ANOVA), including the lack of fit, correlation coefficient (R^2), the Fisher test value (F -value) and the value of " $Prob > F$ ". The optimum values of selected dependent variables were obtained by solving the regression equation and analyzing the response surface contour plots. As a result of these regressions and

plots, additional experiments were also iteratively identified and conducted in triplicate so as to verify the predicted optimize conditions.

2.8. Elemental Analysis, Scanning Electron Microscopy, and Optical Microscopy

The C, H, N, and S contents of the raw materials were monitored with an EA 1110 Fisons elemental analyzer. Morphological properties of the samples were ascertained by using a Nova NanoSEM™ 630 scanning electron microscope (SEM) and optical microscopy. For SEM analysis, a thin layer of iridium was sputter-coated on the SEM specimens under high vacuum; and these specimens were mounted onto a standard SEM holder with conducting carbon tape.

Preparation of polished specimen was required for optical microscopy. For optical microscopy work, the test specimens were mixed with cold-setting epoxy resin, the mixture was packed into a cylindrical PVC mold, which was then vacuumed so as to eliminate air bubbles. When the epoxy hardened, the cylindrical sample was removed from the mold and one end was ground through # 400 and 600 SiC paper grit, and polished using 0.3 micron alumina polishing slurry on a high nap cloth, followed by polishing with a 0.05 micron polishing slurry on a silk surface. Specimens were desiccated overnight before analysis. Polished surfaces were inspected using an oil immersion objective at 625X magnification in white-light with a Zeiss Universal research microscope using a 40X Antiflex objective, and then the photomicrographs were prepared using a digital Zeiss AxioCam camera.

3. Results and Discussion

3.1. First Round of Experiments: Effect of Baking Rate and Cooling Rate on Properties of Baked Samples

In our first round of experiments, the authors appraised three baking protocols: protocol A (52 hours), B (120 hours), C (308 hours) and D (480 hours). As presented in Fig. 2, these protocols all involved gradually ramped-up temperature from ambient, a slightly higher ramping rate above 500 °C, a crest at 800 °C, then abrupt or gradually ramping-down after reaching the crest. The authors accelerated the ramping rate above 500 °C, because we had previously discerned that the thermal decomposition of hybrid binder primarily takes place within the temperature range of 150 to 500 °C. It is in this thermal range where large amount of gaseous products evolve, including H₂O, CO, CO₂, NH₃, formaldehyde, methanol, methane, phenolic compounds, etc.

These preliminary experiments involved two green composite recipes/ hot-pressing protocols: Sample 1 employed 8% lignin, 6% collagen, 86% petroleum coke (where 29.75% of the petroleum coke was fines and 70.25% of the petroleum coke was particles) (dry weight basis); and hot-pressing at 350 °C, 60MPa, for 2 hours. Sample 2 employed 15% lignin, 6% collagen, 79% petroleum coke (including 30% fines plus 70% particles) and additives; and hot-pressing at 400 °C, 45MPa, for 2 hours. All sample baking and tests were conducted in triplicates.

For both green composite samples, the Protocol C baking process yielded baking products with the highest apparent density (1.67 g/mL), lowest electrical resistivity (200-525 μΩm), lowest puffing (3.5-5.7%), and lowest mass loss during baking (7.5-8.5%) (see Fig. 3). Notably, the prolonged cooling rates enabled the secondary reactions to occur at the prolonged high temperatures [30], and this diminished apparent density while increasing puffing. As a result of

these preliminary results, the authors used solely protocol C for all subsequent baking experiments. In summary, this was a baking rate of 0.04 °C/min to 500 °C, then 0.07 °C/min to 800 °C; then cooling rate of 1.08 °C/min for a total of 308 hours (13 days).

Fig. 3 - Effect of baking rate and cooling rate on properties of baked samples (Sample 1: 8% lignin, 6% collagen, 86% petroleum coke (including 29.75% fines plus 70.25% particles) (dry weight basis) , pressure 60 MPa, heating temperature 350°C, soaking time 2h; Sample 2: 15% lignin, 6% collagen, 79% petroleum coke (including 30% fines plus 70% particles), pressure 45 MPa, hot-pressing temperature 400°C, soaking time 2h).

3.2. Hot-Pressing for Green Samples: Response Surface Optimization

Subsequent rounds of experiments focused on the recipes and protocol for hot-pressing the green composite samples. The first stage of these appraised responses following hot-pressing under two extremes of 6 parameters: lignin content (2 or 24%), collagen content (2 or 10%), petroleum coke fines (20 or 80%), pressure (30 or 75 MPa), hot-pressing temperature (100 or 400 °C), and soaking time (1 or 4 hours) (see [Table S1 in Support Information](#)). The resultant “response” was the apparent density of the green composites and subsequent baking products (baked by protocol C); and these response were plotted as half-normal probability plots ([Figure S2a and S2b](#)), and Pareto charts ([Figure S3a and S3b](#)). On the basis of Pareto charts results, only lignin content, collagen content, petroleum coke fines content, and hot-pressing temperature were significant effects that were regarded as the independent variables for the subsequent BBD experimental plan.

Next, for each of these six variables, single factor experiments were employed where one parameter was varied while keeping all others constant at the point corresponding to the maximum apparent density of the green composite. As shown in [Figure S4](#), these showed that the highest baked product apparent density reached 1.67 g/mL. The most favorable results occurred with 10-15% petroleum coke fines, 4-6% collagen, 10-14% lignin, 15-30 MPa pressure, 400 °C hot-pressing temperature, and 2-3 hour soaking time. We note that our hot-pressing oven could not exceed 400 °C.

As the next step, the authors used these independent variables in three-level experiments for the BBD experimental plan of [Table 3](#). This test plan included five replicates at the center point. The baked product apparent densities for these conditions are also presented in [Table 3](#). At this “center point” corresponding to 11% lignin, 6% collagen, 20% petroleum coke fines, 375 °C hot-

pressing temperature, 30 MPa pressure, and 2 hour soaking time. The response apparent density was 1.594 ± 0.016 g/mL. This narrow standard deviation reflected the tight reproducibility.

Table 3 - Box-Behnken Design with five replications at the center points: baked product apparent density response to various parameters.

Run	Lignin (X ₁ , %)	Collagen (X ₂ , %)	Petro coke fines (X ₃ , %)	Hot-pressing temp. (X ₄ , °C)	AD [#] baked (Y ₂ , g/mL)	Puffing during baking (Y ₃ , %)
1	11	6	30	400	1.65	5.09
2	11	10	10	375	1.52	11.51
3	11	6	10	400	1.64	2.79
4	11	2	20	400	1.65	7.43
5*	11	6	20	375	1.62	9.65
6	2	6	10	375	1.50	8.06
7	2	6	20	400	1.52	12.72
8	20	6	20	350	1.52	3.39
9	11	10	20	400	1.63	6.22
10	11	2	10	375	1.62	4.61
11*	11	6	20	375	1.60	7.73
12	2	10	20	375	1.31	18.93
13	11	10	30	375	1.48	5.22
14	2	6	20	350	1.35	8.32
15	11	2	30	375	1.63	7.11
16*	11	6	20	375	1.59	8.23

17	20	6	30	375	1.52	2.39
18*	11	6	20	375	1.57	8.45
19	20	6	20	400	1.59	2.05
20	11	6	30	350	1.52	6.92
21	11	6	10	350	1.52	4.40
22	20	2	20	375	1.57	7.39
23	11	2	20	350	1.53	8.02
24	2	6	30	375	1.43	9.54
25	2	2	20	375	1.39	7.81
26*	11	6	20	375	1.59	8.56
27	20	6	10	375	1.50	0.45
28	11	10	20	350	1.48	7.71
29	20	10	20	375	1.54	2.01

AD, apparent density, as determined by Archimedes' protocol.

The Table 3 results were appraised by a quadratic model; and its terms in the form of analysis of variance (ANOVA) are presented in Table 4. The P value ($Prob > F$) lower than 0.05 generally denotes that this parameter is significant at a 95 % confidence level. It is clear from the table that the quadratic model (equation (1) below) was statistically significant as the Fisher test value (F -value) with a very low P value [$(Prob > F) < 0.0001$]. Contrary to the other terms in this model, the linear terms of lignin (X_1 , %), collagen (X_2 , %), heating temperature (X_4 , °C) and the second-order term of lignin (X_1^2) were significant with [$(Prob > F) < 0.05$]. In traditional optimization protocols, the terms with P value higher than 0.05 can be ignored. However, in this present work, the insignificant terms, especially the two-level interactions, were still maintained to study the influence on the response (discussed later). Moreover, the lack of fit was observed to be insignificant [$(P_{lack\ of\ fit} < F) = 0.0549$], implying that there was good adequacy of fit of the model. The statistical significance of the quadratic model was also confirmed by the correlation coefficient of the model ($R^2 = 0.9061$), which indicated that only 9.39 % of the variability in the response was not explained by the model. Simultaneously, both the value of the adjusted correlation coefficient (adjusted $R^2 = 0.8122$) and the coefficient of variation (C.V. = 2.46 %) were found to be adequate in representing the experimental data.

Based on the above results, application of ANOVA analysis offers the regression equation between the independent variables and the apparent density of baked product, which was computed as follows:

$$Y_2 \text{ (g/mL)} = 1.590 + 0.062 X_1 - 0.036 X_2 - 0.006 X_3 + 0.063 X_4 + 0.012 X_1 X_2 + 0.023 X_1 X_3 - 0.025 X_1 X_4 - 0.012 X_2 X_3 + 0.008 X_2 X_4 + 0.003 X_3 X_4 - 0.100 X_1^2 - 0.029 X_2^2 - 0.006 X_3^2 + 0.003 X_4^2 \quad (1)$$

Table 4 - ANOVA for response surface quadratic model.

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Significance
Model	0.19	14	0.014	9.65	< 0.0001	S^a
X ₁	0.046	1	0.046	32.03	< 0.0001	S
X ₂	0.015	1	0.015	10.82	0.0054	S
X ₃	4.08E-04	1	4.08E-04	0.29	0.6008	NS^b
X ₄	0.048	1	0.048	33.79	< 0.0001	S
X ₁ X ₂	6.25E-04	1	6.25E-04	0.44	0.5185	NS
X ₁ X ₃	2.03E-03	1	2.03E-03	1.42	0.2530	NS
X ₁ X ₄	2.50E-03	1	2.50E-03	1.75	0.2065	NS
X ₂ X ₃	6.25E-04	1	6.25E-04	0.44	0.5185	NS
X ₂ X ₄	2.25E-04	1	2.25E-04	0.16	0.6971	NS
X ₃ X ₄	2.50E-05	1	2.50E-05	0.018	0.8965	NS
X ₁ ²	0.071	1	0.071	50.12	< 0.0001	S
X ₂ ²	5.33E-03	1	5.33E-03	3.74	0.0735	NS
X ₃ ²	2.47E-04	1	2.47E-04	0.17	0.6836	NS
X ₄ ²	4.31E-05	1	4.33E-05	0.030	0.8641	NS
Residual	0.020	14	1.43E-03			
Lack of Fit	0.019	10	1.86E-03	5.64	0.0549	NS
Pure Error	1.32E-03	4	3.30E-04			
Cor. Total	0.21	28				
Std. Dev.	0.038		R-Squared	0.9061		
Mean	1.54		Adj R-Squared	0.8122		
C.V. %	2.46		Pred R-Squared	0.4852		
PRESS	0.11		Adeq Precision	11.712		

^a S, significant; ^b NS, not significant.

The predicted plot for apparent densities of baked products using equation (1) were illustrated together with the experimental data in Fig. 4. The observed scatter of points are distributed around the straight line, with fit to this predicted model reflecting the satisfactory consistency between these values.

Fig. 4 - DESIGN-EXPERT plot. Experimental values for apparent density (g/mL) of baked product versus values (g/mL) predicted by Equation (1).

As another way of presenting this data, the corresponding response surface contour plots of the RSM are shown in Fig. 5-7, which are diagrammed as a function of two independent variables at a time when the other two independent variables were kept at fixed levels. As shown in Fig. 5 and Fig. 6, both figures displayed a symmetrical oval shape contour with the maximum response occurring within the central contour, which confirmed that lignin has a mutual interaction with collagen and petroleum coke fines. These ovals centered at 3.5% collagen, 12.5% lignin, 20% petroleum coke fines, and 400 °C hot-pressing temperature. We note again that the upper bound temperature capacity for this hot-pressing system was 400 °C. This 400 °C is also a fairly common upper bound practical conventionally during this green compositing protocol.

Fig. 5 - DESIGN-EXPERT plot. Response surface contour plot for apparent density of baked product showing the interacting effect of lignin and collagen at conditions of 20% petroleum coke fines, and hot-pressing temperature 400°C.

Fig. 6 - DESIGN-EXPERT plot. Response surface contour plot for apparent density of baked product showing the interacting effect of lignin and petroleum coke fines at conditions of 6% collagen 6%, and hot-pressing temperature 400°C.

Understandably, the apparent density of baked product depends largely on the product of final char yields and mass fraction of each constituent after baking. Increasing the hot-pressing temperature was also beneficial to the advanced release of pyrolytic gaseous products, thus precluding the occurrence of puffing and formation of the cracks during the baking step (see Fig. 7). When the pure lignin was pyrolyzed to 800 °C in the baking furnace, it lost 58 % of its original mass, compared to 75% for collagen. These losses were far more than the 0.27 % mass loss experienced for petroleum coke. Indeed, coke, by definition is carbonaceous material that has already been pyrolyzed at temperatures of 900-1000 °C; and such material would not be expected to experience yet more **significant** mass loss when pyrolyzed at 800 °C yet again.

Fig. 7 - DESIGN-EXPERT plot. Response surface contour plot for apparent density of baked product showing the interacting effect of lignin and hot-pressing temperature at conditions of 6% collagen, and 20% petroleum coke fines.

As a yet further optimization step, the Design-Expert® software utilized the above model and data to discern the recipes and protocols for preparing green composites that would result in a

baked product with the highest density. These were 13.0 % lignin, 3.6 % collagen, 27.4 % petroleum coke fines, and additives; heating temperature 400 °C, soaking time 2 h. Based on the data presented above, verification experiments were conducted in triplicate by incorporating the optimized variables. In these conditions, the experimental apparent density of baked product was 1.667 g/mL; and this was in good agreement with the model prediction (1.671 g/mL) as the error between each other was less than 2 %. These results were considerably more favorable than others have achieved for pitch-based electrodes with or without some additives reported in previous studies (see Table 5).

Table 5 - Apparent densities of baked products based on different binder system, as reported in the literature.

Binders	Puffing inhibitors (wt. %)	Max. baking temp. (°C)	AD [#] baked (g/mL)
Lignin-collagen binder (herein)*	—	800	1.667
Pitch [31]	—	900	1.484
Pitch G [32]	—	1000	1.420
Pitch [33]	1% Na ₂ HPO ₄ • 12H ₂ O	900	1.496
Pitch [34]	3.5% Iron(II) sulfate	900	1.551
Pitch [34]	2% Boric acid	900	1.508
Coal tar pitch [35]	1% NiO	900	1.544
Coal tar pitch [35]	1% C ₆ O	900	1.548
Pitch [31]	1% Fe ₂ O ₃	900	1.523
Pitch [31]	2.5% B ₂ O ₃	900	1.488
Pitch [31]	1% B ₄ C	900	1.515
Pitch [31]	0.8% Boron	900	1.532

[#]AD, apparent density, as determined by Archimedes' protocol; ^{*}Prepared in triplicate herein, when using the statistically-optimized values of 13% lignin, 3.6% collagen, 27.4% petroleum coke fines, 400 °C hot-pressing temperature, and 2-hour hot-pressing soaking time;

3.3. Graphitization

Several of the baked product cylinders with higher apparent densities and lower puffing and cracking were graphitized in the SGL Carbon Co. Ltd. Graphitization units at 2800-3000 °C. These graphitized samples were then monitored for apparent density and electrical resistance by SGL personnel, with results as presented in Table 6. The more favorable graphitized electrodes produced with these lignin-collagen binders hosted an apparent density of 1.51-1.54 g/mL, and an electrical resistance of 27.3-31.7 $\mu\Omega\text{m}$. As per Table 6, the samples selected for graphitization that had been prepared with 10-11% lignin, 6% collagen, and 10 or 20% petroleum coke fines hosted the slightly lower electrical resistances of 24.5-28.7 $\mu\Omega\text{m}$, than did the samples that had been prepared with 12.7% lignin, 3.94% collagen, with 20.4% petroleum coke fines — those exhibited a resistance of 30.3-31.7 $\mu\Omega\text{m}$.

These values compared to the SGL Sigaform® HLM Extruded Graphite of 1.72-1.75 g/mL apparent density and 7.2-10 $\mu\Omega\text{m}$. So, in this first work with these bio-binders, we got close to the target, but not all the way there. Commercially, post-baking pitch impregnation has been used to densify baked product.

Table 6 - Comparison of the results for baked and graphitized samples using bio-binders to SGL Sigriform®.

Carbon source			Pressure (MPa)	Hot- pressing temp. (°C)	Soaking time (h)	AD [#] green (g/mL)	AD baked (g/mL)	Puffing during baking (%)	ER* baked (μΩm)	AD graphite electrode (g/mL)	ER graphite electrode (μΩm)
Lignin (%)	Collagen (%)	Petro coke fines (%)									
Sigriform® HLM Extruded Graphite			—	—	—	—	—	—	—	1.72-1.75	7.2-10
12.70 %	3.94 %	20.43 %	30	400	2	1.87	1.60	8.50	222.91	1.49	31.71
12.70 %	3.94 %	20.43 %	30	400	2	1.84	1.59	7.60	—	1.51	30.35
10 %	6 %	20 %	45	400	2	1.70	1.60	4.16	346.53	1.52	—
10 %	6 %	20 %	45	400	2	1.86	1.63	4.45	—	1.53	27.32
10 %	6 %	20 %	45	350	4	1.81	1.62	3.13	851.90	1.52	—
11 %	6 %	10 %	30	400	2	1.70	1.64	2.79	297.25	1.54	—
11 %	6 %	10 %	30	400	2	1.85	1.58	7.14	—	1.5	24.57
11 %	6 %	10 %	30	400	2	1.87	1.60	8.51	145.00	1.48	28.68
15 %	6 %	40 %	30	400	2	1.79	1.61	9.30	357.53	1.48	—
11 %	2 %	30 %	30	375	2	1.74	1.63	7.11	483.48	1.48	—
10 %	6 %	20 %	21	350	2	1.85	1.64	9.84	540.76	1.456	—

AD, apparent density, as determined by Archimedes' protocol; *ER, electrical resistance.

3.4. Puffing Behavior during the Baking Process

Puffing is a significant issue during the baking and graphitization steps; and it is characterized by the focused release of volatilized gases from within the solid matrix. Puffing refers to irreversible volume expansion of the solid; and it is mainly caused by a sudden release of N-, and S-containing gases during baking or graphitization [31, 33-36]. When using lignin and collagen, it can also be related to oxygen-containing gases release, which can be significant. Relative to the bio-binder based electrodes in the present work, puffing can be attributed to the sustained release of pyrolytic gases from lignin and collagen that can occur between 150 and 800 °C during the hot-pressing green process and baking; and also during graphitization. Puffing poses serious consequences, since it may cause the formation of pores and cracks, thus leading to the decrease of apparent density, flexural strength, thermal conductivity and electrical conductivity. Fig. 8 exhibits an array of the various types of cracks that the carbon surface developed when these bio-binders were employed.

Fig. 8 - Surface cracks of favorable green composite (a) and subsequent favorable baked products (b), as compared to unfavorable baked product (c-d)

Following the green hot-pressing protocol, **some of this** puffing could be avoided by pre-lubricating the mold, and the product green composite hosted a smooth finish as shown in Fig. 8a. Then during the baking step, favorable conditions yielded a smooth product as in Fig. 8b, but unfavorable protocols yielded a surface with horizontal cracks, such as in Fig. 8c and d. In that these horizontal cracks lengthened the vertical dimension of the cylinder specimen, they were **also** measured as causing “puffing”. Also, the widths of cracks could be measured, and their cumulative sum for a given cylinder specimen could be compared to the overall extent of total puffing. For example, as presented in Figure 9 and Table 7, when specimens experienced 2%

puffing during baking, the visible cracks that were cumulatively measured represented 5-6% of puffing-lengthening. In comparison, with 9% puffing, visible cracks accounted for 10-25% of the puffing-lengthening.

Fig. 9 - The relationship between puffing and crack during the baking process.

Table 7 – The relationship between puffing and crack

Run	Lignin (%)	Collagen (%)	Petro coke fines (%)	Pressure (MPa)	Hot-pressing temp. (°C)	Soaking time (h)	AD [#] green (g/mL)	AD baked (g/mL)	Puffing during baking (%)	The ratio of crack to puffing (%)
S7	2	2	20	75	400	4	1.82	1.63	8.86	15.71
RS14	2	6	20	30	350	2	1.69	1.35	8.32	15.36
RS24	2	6	30	30	375	2	1.73	1.43	9.54	18.04
S2	2	10	20	30	400	1	1.85	1.68	4.70	11.37
Bu18	10	6	20	21	350	2	1.85	1.64	9.84	8.81
BU26	10	6	20	45	250	2	1.68	1.56	9.50	9.79
Bu27	10	6	20	45	300	2	1.74	1.47	12.37	12.96
Bu23	10	6	20	45	350	2	1.90	1.55	11.51	12.62
BU28	10	6	20	45	400	2	1.70	1.60	4.16	5.92
RS10	11	2	10	30	375	2	1.77	1.62	4.61	7.13
RS23	11	2	20	30	350	2	1.77	1.53	8.02	8.93
RS3	11	6	10	30	400	2	1.70	1.64	2.79	3.92
RS5	11	6	20	30	375	2	1.86	1.62	9.65	9.83
RS20	11	6	30	30	350	2	1.83	1.52	6.92	11.16
RS1	11	6	30	45	400	2	1.78	1.65	5.09	7.02
RS2	11	10	10	30	375	2	1.74	1.52	11.51	17.65
RS13	11	10	30	30	375	2	1.68	1.48	5.22	11.51
RS28	11	10	20	30	350	2	1.63	1.48	7.71	18.25
RS9	11	10	20	30	400	2	1.77	1.63	6.22	12.43

BU12	14	4	20	21	350	2	1.81	1.66	9.04	14.20
BU14	14	8	20	21	350	2	1.80	1.54	7.19	14.27
BU11	14	10	20	21	350	2	1.77	1.45	6.55	6.75
BU5	15	6	10	45	400	2	1.81	1.57	6.79	16.42
BU6	15	6	50	45	400	2	1.78	1.59	9.24	21.56
RS22	20	2	20	30	375	2	1.76	1.57	7.39	8.67
RS8	20	6	20	30	350	2	1.74	1.52	3.39	11.07
RS19	20	6	20	30	400	2	1.70	1.59	2.05	5.55
RS29	20	10	20	30	375	2	1.62	1.54	2.01	6.27
S15	24	2	80	75	100	4	1.45	1.10	9.18	24.63
S13	24	10	20	30	100	4	1.68	1.20	4.20	12.88
S16	24	10	80	75	400	4	1.36	1.28	8.89	19.88

[#] AD, apparent density, as determined by Archimedes' protocol.

In order to further understand the occurrence and development of puffing during the baking process, Box-Behnken Design and quadratic model were also employed. This model inputted the puffing results in [Table 3](#), to determine the simple and combined effects of four independent variables (i.e. lignin content, collagen content, petroleum coke fines content, and hot-pressing temperature) on the puffing during the baking process. The following equation is the ultimate model resulting from AVONA analysis in terms of coded independent variables for puffing:

$$\text{Puffing (Y}_3, \%) = 8.52 - 3.97 X_1 + 0.77 X_2 + 0.37 X_3 - 0.20 X_4 - 4.13 X_1 X_2 + 0.12 X_1 X_3 - 1.44 X_1 X_4 - 2.20 X_2 X_3 - 0.23 X_2 X_4 - 0.055 X_3 X_4 - 0.55 X_1^2 + 0.81 X_2^2 - 2.42 X_3^2 - 1.55 X_4^2$$

The predicted versus actual plot for puffing has been shown in [Fig. 10](#). The observed points on this plot reveal that the actual values are distributed relatively near to the straight line in this case, indicating good agreements between the actual and predicted values. The statistical significance of the model and its items were also evaluated by the analysis of variance (ANOVA) which was illustrated in [Table 8](#). The calculated Fisher test value corresponding to puffing response was 11.94, with a very low probability value [$(Prob > F) < 0.0001$] lower than 0.05, implying the significance at 95% confidence level. The insignificant lack of fit [$(P_{lack\ of\ fit} < F) = 0.0549$] and high correlation coefficient ($R^2 = 0.9061$) were observed, which still maintained to support the representation of this predicted model.

Fig. 10 - DESIGN-EXPERT plot. Experimental values for puffing (%) during the baking versus values (%) predicted by Equation (2).

Table 8 - ANOVA for response surface quadratic model.

Source	Sum of Squares	DF	Mean Square	<i>F</i> Value	Prob > <i>F</i>	Significant
Model	355.31	14	25.38	11.94	< 0.0001	S ^a
X ₁	189.61	1	189.61	89.19	< 0.0001	S
X ₂	7.1	1	7.1	3.34	0.089	NS ^b
X ₃	1.65	1	1.65	0.78	0.3932	NS
X ₄	0.5	1	0.5	0.24	0.6338	NS
X ₁ X ₂	68.06	1	68.06	32.02	< 0.0001	S
X ₁ X ₃	0.053	1	0.053	0.025	0.8769	NS
X ₁ X ₄	8.24	1	8.24	3.87	0.0691	NS
X ₂ X ₃	19.32	1	19.32	9.09	0.0093	S
X ₂ X ₄	0.2	1	0.2	0.095	0.7621	NS
X ₃ X ₄	0.012	1	0.012	0.005692	0.9409	NS
X ₁ ²	1.96	1	1.96	0.92	0.3531	NS
X ₂ ²	4.3	1	4.3	2.02	0.177	NS
X ₃ ²	38.02	1	38.02	17.89	0.0008	S
X ₄ ²	15.58	1	15.58	7.33	0.017	S
Residual	29.76	14	2.13			
Lack of Fit	27.77	10	2.78	5.58	0.0561	NS
Pure Error	1.99	4	0.5			
Cor Total	385.07	28				
Std. Dev.	1.46		R-Squared	0.9227		
Mean	6.99		Adj R-Squared	0.8454		
C.V. %	20.86		Pred R-Squared	0.5765		
PRESS	163.07		Adeq Precision	16.067		

^a S, significant; ^b NS, not significant.

It is noteworthy that inspection of the AVONA results here indicates that except for the linear term of lignin (X_1), the factors that posed the most significant effect on puffing were the interacting effects such as lignin $\times$ collagen ($X_1 X_2$), collagen $\times$ petroleum coke fines content ($X_2 X_3$), and the second-order terms of petroleum coke fines content (X_3^2) and hot-pressing temperature (X_4^2). This was distinct from the results obtained for apparent density response. In light of this, the authors modeled contour plots of the RSM, as presented in [Fig. 11-13](#); and these were applied to elucidate both the main and the interaction effects of these variables on puffing behavior. As can be seen from [Fig. 11](#), increasing the addition of lignin at a fixed level of collagen content favorably decreased the puffing behavior. In comparison, puffing increased sharply when the collagen content increased while lignin content remained low (lower than approximate 11 %). These distinctions could be attributed to the differences in pyrolytic characteristics of lignin and collagen. Since the lignin contains various chemical bonds and functional groups, its thermal degradation thus proceeded over an extremely wide temperature range (100-800 °C), leading to the formation of porous coke. This specific porous structure is undoubtedly helpful in releasing the pyrolytic gaseous products and reducing the puffing behavior. Collagen, however, includes not only carbon, oxygen, and hydrogen, but also nitrogen in various amino acids. Thus, upon pyrolysis, collagen could release considerable nitrogen as ammonia and other gases in a relatively narrow temperature range of 200-350 °C, resulting in the occurrence of puffing and cracks. Furthermore, intriguingly, when the amount of lignin exceeded 11 %, the puffing exhibited a modeled declining tendency with the increase of collagen. Presumably the presence of lignin favored to create effective “breathing channels” from the surface to the center for collagen-derived gas emission.

Fig. 11 - DESIGN-EXPERT plot. Response surface contour plot for puffing showing the interacting effect of lignin and collagen at conditions of petroleum coke fines 20%, heating temperature 400°C.

Fig. 12 - DESIGN-EXPERT plot. Response surface contour plot for puffing showing the interacting effect of lignin and heating temperature at conditions of collagen 6%, petroleum coke fines 20%.

Fig. 13 - DESIGN-EXPERT plot. Response surface contour plot for puffing showing the interacting effect of lignin and petroleum coke fines at conditions of collagen 6%, heating temperature 400°C.

Fig. 12 denotes the interaction effect of the lignin content and hot-pressing temperature on the puffing. The interaction characteristic appears to be similar with an elongated U-shaped plots, i.e. in one axis, there is a linear decrease in puffing, however, on the other axis, the puffing increased up to only a certain point, then decreased thereafter. This result reflects that the optimum hot-pressing temperature to be used in preparing green composites that favor lower puffing is 400 °C. Generally speaking, higher hot-pressing temperature corresponded to more pyrolysis gases released during hot-pressing; and these gases came from lignin and collagen. The gas release presumably relieved stress during the subsequent baking process to a certain extent. However, employing a high hot-pressing temperature may not offer the most favorable strategy since the highest puffing occurred at intermediate temperatures, per TGA analyses [28]. We anticipated that the most favorable approach for achieving low puffing inhibition was to control the formation of effective “breathing channels” under the proper temperature and the sustained

release of the pyrolytic gaseous products. Although low hot-pressing temperature (300 °C) resulted in low-puffing during the hot-pressing step, it left too much potential for releasing pyrolytic gaseous products during the baking process. And this thus resulted in the decreased apparent density of baked products.

An important interaction characteristic was also observed between puffing and the proportion of petroleum coke fines ([Fig.13](#)). Per this model, about 20% coke fines incurred the most puffing; and either more or less fines diminished puffing. When including fewer petroleum coke fines (lower than 15%, say) the fines did not fill all the vacancies between petroleum coke particles; and this meant that the pyrolysis gases could escape through these vacancies. Alternatively, when coke fines were higher than say 25%, each fine coke particle and surrounding agglomerate of lignin and collagen released the gases internal to itself more readily – and at lower temperatures while the composite was still viscous and malleable, thus resulting in less gas release and puffing when the composite became rigid.

The rate of gas evolution was another factor that affected the extent of puffing, as demonstrated in [Fig. 3](#). Lower heating rate, especially in the temperature range corresponding to the main pyrolysis stage, tended to reduce the mass loss caused by hybrid binders pyrolysis and protect the carbon bodies against the sudden shock of gas pressure, thus reducing puffing phenomena.

3.5 The Morphologies of Specimen Containing Various Contents of Hybrid Binder

SEM micrographs shown in [Fig. 14](#) reveal the structural differences among the binder compositions in green composites ([see in Table 9](#)). A green composite, prepared by hot-pressing technology, is a composite of filler and binder derived cokes. The filler petroleum coke particles

can be considered to be aligned almost parallel to the pressure axis, showing anisotropy parallel to level cross-section. In comparison the hybrid binder layers obtained from lignin and collagen distributed randomly in the interior and surface of petroleum coke particles. With increasing temperature, the gas products from the hybrid binders are generated so as to build up a pressure that has exactly the reverse effect on this idealized structure. Even though puffing is also inherently observed within individual binder and petroleum coke particles, extents are usually much less than briquette form. Extents of puffing are thus strongly dependent upon the approach to pressure release, namely the formation of “breathing channels” in the baked product, which was highly correlated with the addition of hybrid binders.

Fig. 14 - SEM micrographs of the green composites prepared at 350°C: (a) lignin 4%, collagen 6%, petroleum coke fines 20%; (b) lignin 10%, collagen 6%, petroleum coke fines 20%; (c) lignin 14%, collagen 10%, petroleum coke fines 20%.

Table 9 – Physical properties of baked product response to various parameters

Lignin (%)	Collagen (%)	Petro coke fines (%)	Pressure (MPa)	Hot-pressing temp. (°C)	Soaking time (h)	AD [#] green (g/mL)	AD baked (g/mL)	Puffing during baking (%)
4	6	20	21	350	2	1.72	1.49	11.53
10	6	20	21	350	2	1.85	1.55	8.51
14	10	20	21	350	2	1.77	1.45	6.55

[#] AD, apparent density, as determined by Archimedes' protocol.

As can be seen from Fig. 14, the presence of hybrid binder gave rise to a structure that was comprised of viscous layers covering the surface of the petroleum coke and different sizes of aggregates. The aggregates were comprised of various chars derived from lignin, collagen and / or petroleum coke. Specifically, when 4% lignin was bindered to 20% petroleum coke fines with 6% collagen, the lesser amount of hybrid binder did not form a continuously-binding char-bridge that could have filled the vacancies between petroleum coke particles (see Fig. 14a). Also, there were still a certain number of hybrid binders randomly distributed. In this context, the composite structure seemed relatively fragile. The pyrolysis gases were unable to release via available structural channels, which tended to cause the overexpansion of volume and the formation of cracks. This corresponded the high puffing value.

The homogeneous ingredients with the right proportions of hybrid binder and petroleum coke favorably to created effective “breathing channels”. These channels could extend from the surface to the cylinder’s center for gas emission. With the increasing of lignin addition from 4% to 10%, the hybrid binders spread broadly into spaces between coke grains, and exhibited multilayer growth (see Fig. 14b, yellow oval). These observations contributed to the improved compactness, greater smoothness, and higher apparent density for these composite structures. Further, higher proportion of hybrid binders also facilitated greater adherence to the petroleum coke, and thus augmented binder dispersion over coke particles. This enhanced the formation of vapor release channels, and apparently decreased puffing.

The continued increase of hybrid binders led to significant morphological changes (see Fig. 14c) in the thickness of the binding layers and the sizes of aggregates. As lignin and collagen were main source of the pyrolytic gaseous products, the weight loss of hybrid binders thus had a profound effect on the physical and mechanical properties. Correspondingly, the baked product

with more hybrid binders exhibited a lower apparent density. However, contrary to the general conception that more puffing occurred under the condition of more pyrolytic gaseous products available to be released, lower puffing with higher content of hybrid binders was observed. This phenomenon could be attributed to the formation of vapor release channels if excess hybrid binders were applied at the expense of apparent density.

Fig. 15 shows the optical micrographs of various types of electrodes. As the hot-pressing process occurred, the hybrid binder particles had softened, melted and fused into a matrix. From the color areas in Fig. 15a, it is evident that lignin (orange region) and collagen (blue region) exhibited thin layers that covered the surface of petroleum coke (beige region) and partly penetrated into the pore structure within petroleum coke grains. Due to the release of the pyrolytic gaseous products within the binder matrix, there were still a few residual porosities in some regions, indicated by the presence of black spots in different sizes. At the stage of carbonization (see Fig. 15b), with the increasing of pyrolysis behavior, the structural porosity also increases accordingly as a result of the gas emission. Meanwhile, the large fused ring networking attributing to the synergistic effect between lignin and collagen provided a binding system for petroleum coke and created a new turbostratic structure together, which included the presence of both graphitic or highly ordered carbon, and amorphous or less ordered carbon. The graphite electrode image exhibited mutual orientation of the graphite crystallites, with multi-layers of parallel structures in cross-section (see Fig. 15c). Under the influence of thermal movements, graphite crystallites constantly grew along the direction of the stresses, leading to the occurrence of the bending and compression deformation (see white oval). Both of these changes caused the parallel structure to shrink. This densified the graphite structure, but may have also imparted shrinkage cracks that resisted electrical conductivity.

Fig. 15 - Optical micrographs of various types of carbon materials: (a) green composite, (b) baked product and (c) graphite electrode. The recipes and protocols: 20% lignin, 4% collagen, 40% petroleum coke fines.

3.6 Raman Spectroscopy

Raman spectra for these thermally treated composites have been shown in Fig. 16, following thermal treatments of 500 °C, 800 °C, and graphitization at 2800-3000 °C. The first two had been subjected to these temperatures for 3 hours. The graphitized sample was graphitized at SGL Carbon for the course of about a month. As can be seen, the 500 °C exhibited the largest peak area ratio of I-D-band / I-G-band, whereas the graphitized sample exhibited the lowest D/G area ratio. Indeed, for the graphitized samples, the D-band in the 1300-1400 cm^{-1} range was almost non-existent, inferring scant disorder. We also note that in the 2700 cm^{-1} range, the ν 3D band was greatest for the graphite sample, indicating the highest three-dimensional interaction for that sample.

Fig. 16 - First and second order Raman spectra of the carbon materials obtained from the mixture of lignin, collagen and petroleum coke: lignin 20%, collagen 4%, petroleum coke fines 40%, petroleum coke particles 60%. The 500 or 800 °C samples had been pyrolyzed for 3 hours.

4. Conclusions

This research has provided a novel approach for preparing specialty graphite electrodes, and it points to an opportunity for using renewable biomaterials, such as lignin and collagen, as alternatives to traditional coal tar pitch or petroleum pitch. Response surface methodology (RSM) coupled with Box-Behnken Design (BBD) was successfully demonstrated to determine the optimum parameters for green composite fabrication, where the highest apparent density of 1.67 g/mL and 6.2% puffing was achieved at the optimum conditions of 13.0% lignin, 3.6% collagen, 27.4% petroleum coke fines plus additives; while using a hot-pressing temperature of 400 °C, pressure 30 MPa, and soaking time 2 h. Alternatively we achieved a baked product with 1.56 g/mL density and 1.67% puffing when using 2% collagen, 24% lignin, 20% petroleum coke fines and additives; with baking following hot-pressing of 75 MPa at 400 °C for 1 hour. We note that the resulting apparent density of baked product was found to be superior to those reported by others in previous studies with similar biomaterials. After this baked product was graphitized, the resulting graphite electrodes hosted an apparent density of 1.51 g/mL and an electrical resistance of 30 $\mu\Omega\text{m}$. This (first attempt) was slightly out of the range of a specialty graphite specification of 1.72-1.75 g/mL apparent density and 7.2-10 $\mu\Omega\text{m}$ resistance. The baked and graphitized samples also exhibited some puffing.

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graphitization of samples, as coordinated by Thomas Kraus of SGL Group – The Carbon Company, Morganton, North Carolina.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, and includes Fractional factorial design, Half-normal probability plots, Pareto charts, and Single factor experiments.

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