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Thermally stable and tough coatings and films using vinyl silylated lignin

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ABSTRACT

We modified lignin, a renewable biomacromolecule with high carbon density, with silicon-containing vinyl groups via a highly efficient silylation reaction that achieved ~ 30% substitution of lignin's hydroxyl units. This exothermic process was carried in the melt state, *in situ*, in a reactive extruder. ^{1}H, ^{13}C, ^{31}P NMR and FTIR confirmed the success of the silylation and were used to access the reactivity of the vinyl silylated lignin for copolymerization with polyacrylonitrile (PAN). Copolymers of the unmodified lignin and PAN were also produced as a reference. Importantly, the rheological behavior of the copolymers of lignin and PAN were suitable for application in surface coating and films that were not possible if lignin or physical mixtures of lignin and PAN were used. Glass surfaces were treated via solution casting followed by oven drying, yielding films that were evaluated as far as their morphology (SEM) and thermal properties (TGA and DSC). The films produced with copolymers based on vinyl silylated lignin displayed a Young modulus of 486 MPa, an ultimate stress of 18 MPa and strain of 55 % (DMA). These results indicated a much tougher system than that achieved after copolymerization of the unmodified lignin with PAN (ultimate stress and strain of less than 10 MPa and 10 %, respectively). Overall, the introduced SiC and SiOC bonds improved lignin macromolecular mobility and facilitated its processability due to the remarkably low viscosity of the system. Our results show promise opportunities for lignin utilization as a precursor of copolymers, as illustrated here with PAN, towards flexible films.

KEYWORDS. Lignin; reactive extrusion; vinyl silylated lignin; polyacrylonitrile; copolymers; films; coatings.

INTRODUCTION

Polyacrylonitrile (PAN) is typically synthesized by free radical polymerization of acrylonitrile to form a $(C_3H_3N)_n$ linear structure. Given its properties such as lightweight, thermal stability, strength, stiffness, and electrical conductivity, PAN has been converted into a large variety of products, including acrylic[1] and carbon fibers[2], carbon films[3], carbon foams[4], and ultrafiltration membranes[5], among others. As a precursor of carbon fibers, PAN represents over 90 % of the supply while the rest is mainly pitch.[6-7] Because the strong chemical bonding between nitrile (CN) groups, PAN resists most organic solvents and does not melt before degradation.[8-9] As a result, PAN-based precursors are not cost-effective for direct extrusion; instead, wet spinning or plasticizer-assisted melt spinning are among the preferred routes.[10] The high cost of PAN precursor production limits its use to high end applications, which primarily includes carbon fibers for high performance composites, aerospace and sporting materials.[11] In fact, PAN cost has been reported to be as high as $15 per pound in 2013, according to ICIS Chemical Business.[12] The high raw material cost of PAN-based materials limits its use to only high-end applications.

In order to find a less expensive alternative, many synthetic polymers have been investigated. Polyacetylene (PAc), for example, can be used to prepare helical carbon nanofibril thin films.[13] Likewise, taking advantage of its low cost, polyethylene (PE) has been used in the manufacture of high density composite films reinforced with carbon nanotubes.[14] Some grades of carbon fibers can be produced from polymers such as polyvinyl chloride[15], polyethylene[16], and polyacetylene.[17] Numerous PAN-based copolymers or blends are being investigated.[18] Generally, high C/H ratio structures, such as aromatic rings, result in material with high carbon. However, most conventional polymers lack aromatic rings or have relative low carbon yields, which can increase the cost for further thermal treatment or processing.[10] This is in contrast to PAN-based carbonized materials, which have high carbon content and can be processed easily into end-products with high carbon yields.

It is not surprising that renewable biopolymers with high carbon density have been considered for combination or substitution of PAN. The lignin macromolecule, which is rich in aromatic units, is available in aqueous dispersions as a byproduct of the cellulosic pulp production, where it is often utilized for energy co-generation. In fact, less than 2 % of the lignin industrially available is used for non-energy purposes.[19] This includes around 1.1 million ton per year of different types of lignins that are produced from (wood and non-wood) fiber digestion processes. Most of this amount, approximately 1 million ton/y, comprise lignosulfonates, which are mainly produced from acid sulfite pulping processes and are used as emulsifiers and dispersants, among others.[20-22] The remaining, about 100,000 ton/y are produced by the kraft process.[23] Only limited quantities of organosolv lignins are produced every year.[24] However, a wide range of potential applications of lignins have motivated work in fractionation processes based on kraft black liquor. In 2013, for example, a full-scale commercial LignoBoost plant was founded by Domtar Inc. in North Carolina, USA to produce 75 tonnes per day of kraft lignin.[25] Later on, West Fraser Timber Company in Cananda and Stora Enso in Finland installed LignoBoost processes to produce 30 and 50 tonnes per day of kraft lignin, respectively.[26] All in all, there is promise that kraft lignins will be available in commercial quantities to enter the market for high-value applications.

The carbon content of the kraft and organosolv lignins is about 62 and 63%, respectively.[27] Such carbon content is quite competitive if compared with that of PAN, 68 % carbon. Therefore, there are good prospects for the isolation of lignin as a cost-effective precursor for carbonized materials. Not only is lignin renewable and inexpensive, but it is partially oxidized and can undergo oxidative thermal stabilization at potentially higher rates than PAN.[28]

Lignin has been considered for the production of lignin-based carbonized fibers.[29] However, while many approaches have been reported,[30-35] the expectations of a robust feedstock toward carbon fibers have not been met. This is due to the relatively low tensile strength and brittleness of the respective products. Thus, further efforts need to be directed toward lignin-based blends or copolymers in order to achieve a good balance between strength and cost. In this context, polyethylene oxide (PEO) has been considered as plasticizer to improve the spinning performance and strength.[33] Likewise, polypropylene (PP)[36] and polyethylene terephthalate (PET)[37] have been used to produce carbon fibers by blending with lignin in order to reach a higher thermal stabilization rate. For PAN-based precursors, lignin has been examined as extender to produce carbon fibers[38] and carbon films.[39] In order to further reduce the cost and improve spinnability and strength, a lignin-acrylonitrile copolymer was effective in producing carbon fibers.[40] However, there still a need for an efficient method to produce predominately lignin-based polymer precursors.

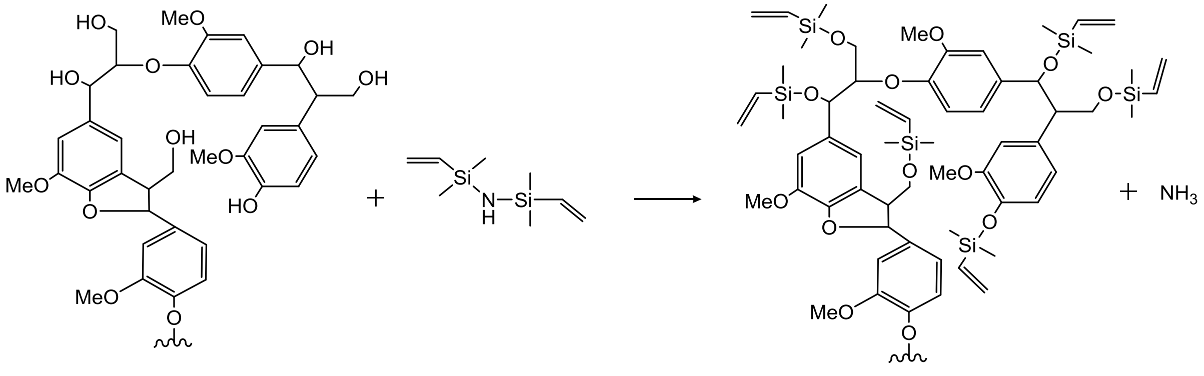
In order to combat some of the challenges outlined above, we investigated using reactive extrusion of industrial kraft lignin and a vinyl-terminated disilazane. The highly efficient vinyl silylation reaction[41] conducted under high shear conditions, allowed for processing in a melt polymer state. It is well known that hexamethyldisilazane (HMDS) will readily react with hydroxyl groups on silica in an exothermic manner.[41] Thus, the –OH groups on lignin were targeted for this same reaction. We propose utilizing 1, 1, 3, 3-Tetramethyl-1, 3-divinyldisilazane (DVDZ), versus HMDS, for substitution of the lignin's hydroxyl groups to open the possibility for subsequent modification via the vinyl functionality. The specific aims of this study were 1) to establish reactive extrusion as a viable methodology to produce vinyl silylated lignin, 2) to determine the reactivity of vinyl silylated lignin (ViSiL) through copolymerization with acrylonitrile, and 3) to evaluate the mechanical and thermal properties of the poly (acrylonitrile-co-ViSiL) films.

MATERIALS AND METHODS

Materials. Industrial pine kraft lignin (Domtar, Plymouth, NC) was purified with 10% solid content in 0.1M HCl solution (pH ~ 1.5). After filtration, the solids were further washed with distilled water with 2 or more rounds. The average molecular weight of the lignin was measured to be ca. 6,200 Da and the hydroxyl groups' content was determined to be > 8 mmol/g.[27] 1, 1, 3, 3-Tetramethyl-1, 3-divinyldisilazane (DVDZ, VWR Radnor, PA) was used in the disilazane reaction. Acrylonitrile (AN), α, α′-azoisobutyronitrile (AIBN, 98%), hydrogen peroxide (H_2O_2, 30 wt% in water), and dimethyl sulfoxide (DMSO, reagent grade) were purchased from Sigma-Aldrich (St. Louis, MO) and used for PAN-lignin copolymerization and dissolution.

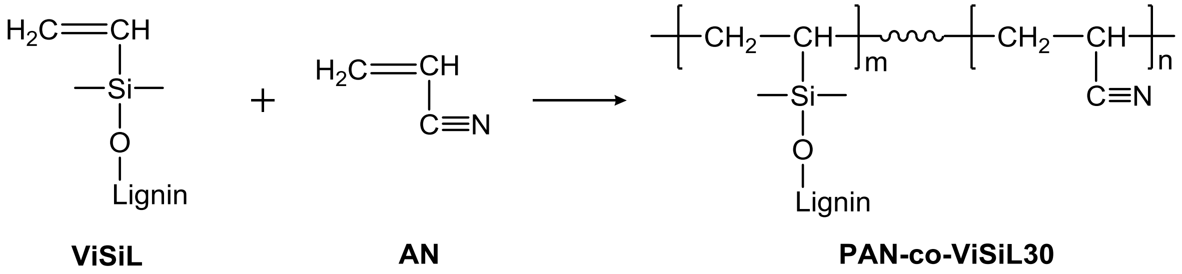
Vinyl silylated lignin (ViSiL). The lignin was functionalized via reactive extrusion to facilitate end-capping of –OH groups via a vinyl silylation reaction (Scheme 1). For this purpose, 6.5 g lignin was premixed with 10 ml 1, 1, 3, 3-tetramethyl-1, 3-divinyldisilazane (DVDZ). The mixture was then introduced in a twin-screw extruder (MC 15, Xplore®, Geleen, Netherlands) operating at 120 °C and at a rotation speed of 120 rpm. The outlet orifice was kept closed for 15 minutes to retain the mixture under circulation in the system and to complete the vinyl silylation reaction. This is an exothermic reaction due to the preference of the silicon atom to associate with the oxygen atom from lignin's –OH groups and the nitrogen's preference to associate with hydrogen.[41-42] Thereafter, the vinyl silylated lignin (ViSiL) was extruded from the reactor and air-dried for 48 hours at room temperature.

Reaction completion was determined by FT-IR (Perkin Elmer Frontier, Waltham, MA) operated in Attenuated Total Reflection (ATR) mode and using 80 scans to generate spectra within the 4000-650 cm^{-1} frequency range with a 4 cm^{-1} resolution. The functional groups were identified according to references.[43] Moreover, ^1H and ^{13}C NMR (Bruker 300 MHz, Karlsruhe, Germany) spectrometry was used for further validation. For this purpose, 85 mg samples were dissolved with 0.7 ml TMS-free DMSO-d$_6$ solvent (Sigma-Aldrich, St. Louis, MO) in a 5 mm NMR tube. 2 mg chromium (III) acetylacetonate was added for complete relaxation of all nuclei.[44] All spectra were obtained with 90° ^{1}H and ^{13}C standard pulse and relaxation delay of 10s and 1.7s, respectively.[45] ^{1}H NMR spectra were collected after 256 scans with the chemical shifts (δ_H) from -4.0 to 14 ppm. ^{13}C NMR spectra were obtained after 10 K scans with the chemical shifts (δ_C) between -40 to 200 ppm. In addition, using the same unit with a ^{31}P probe, the degree of the substitution was determined from the chemical shifts (δ_P) from 130 to 155 ppm.[27, 45] The N-hydroxy-5-norbornene-2, 3-dicarboximide (99 %, VWR, Radnor, PA) was used as an internal standard for ^{31}P NMR. The hydroxyl groups of both lignin and internal standard were phosphorylated at same molar ratio of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (95 %, Sigma Aldrich, St. Louis, MO) in order to quantify the hydroxyl groups in the lignin.[46]



Scheme 1. Vinyl silylation reaction between kraft lignin and divinyl tetramethyldisilazane.

PAN-co-ViSiL copolymerization. Kraft lignin (KL) and ViSiL were copolymerized with acrylonitrile (AN). The copolymerization was conducted using a two-step process.[40] In the first step, 18.7 g of AN and 22 mg AIBN were mixed with 50 g DMSO using magnetic stirring in a 250 ml flask (3 h at 70 °C) within a nitrogen atmosphere in order to favor low molecular weight polymerized AN. The resultant amber solution was cooled down to 50 °C and then 8 g of kraft lignin and 40 g of DMSO were added in the second step. After 15 min mixing, 4.3 ml hydrogen peroxide (30 %) was gradually added to the mixture. The entire system was heated back to 70 °C for another 6 h reaction. The resulting products were poured into deionized water for precipitation. The filtered, final product was dried at 70 °C in a vacuum oven and grinded. The amount of AN and lignin were varied to obtain a given AN/ViSiL ratio in the copolymers (PAN-co-ViSiL). PAN-co-ViSiL10, PAN-co-ViSiL20 and PAN-co-ViSiL30 are used here to indicate 10, 20, and 30 % of ViSiL based on total PAN-lignin copolymer solids, respectively. Likewise, PAN-co-KL30 stands for the copolymer obtained after reaction with kraft lignin (KL) instead of ViSiL, with 30% KL based on total solids. Note that unless indicated otherwise, PAN-co-ViSiL is used to refer in generic terms to AN/ViSiL copolymers, regardless their AN/ViSiL ratio. The synthesized PAN and PAN-co-ViSiL30 copolymers were investigated by ^{1}H NMR and ^{13}C NMR under the same experimental conditions as indicated above for the modified lignin. A possible structure of the PAN-co-ViSiL30 copolymer is displayed in Scheme 2.



Scheme 2. Illustrative molecular structure of PAN-co-ViSiL30 copolymer, noting that *m* and *n* are the respective molar number forming either random or block structures.

PAN-lignin films. The blend of PAN/lignin and PAN-lignin copolymers were dispersed in DMSO at a solids content of 18 %, respectively. The mixtures were moved to a shaker operating at 120 rpm at 70 °C for 24 h. The produced solutions were cast onto a clean glass support by using a glass rod that allowed a film thickness between 0.5 and 1 mm. The wet samples were transferred to a vacuum oven at 70 °C and the films obtained were peeled off manually from the glass substrate.

In order to determine the polymerization reactivity, a hot-pressed copolymer film was prepared. The PAN-Lignin copolymers were grinded into uniform powder. Copolymer powder (5 g) was transferred to the center of a flat round metal plate (diameter of 30 cm). Another same-sized parallel plate was carefully put on it under slow rotation so as to disperse the powders evenly within a round area with diameter around 5 cm. Next, the parallel plates were hot-pressed with a standard bench top press (Carver Inc., Wabash, IN) using 200 °C and 9000 psi for 30 min. The hot-pressed films (~2 mm thickness) were collected off the plates after cooling down.

Solution rheology. The rheology behavior of the casting solutions comprising PAN-lignin copolymers and PAN/lignin blends were analyzed with a TA rheometer (AR-2000, New Castle, DE). A 40 mm steel plate was used with 300 μm gap between the parallel plates. The dynamic viscosity was measured as function of shear rate in the range 0.1-1000 s^{-1} collecting four data points every 10 s^{-1}. For all the casting solutions, the solid content was kept at 18 wt %.

Thermal Properties. The thermogravimetric analysis (TGA) was carried out by using a TA Q500 (TA instrument, Castle, DE) with a platinum pan under nitrogen flow of 50 ml/min. The temperature was raised to 105 °C for moisture removal and then reduced back to 40 °C for equilibrium. Then the samples were heated from 40 °C to 600 °C using a temperature ramp of 10°C/min. TGA profiles were generated as weight percentage (%) change as a function of temperature (°C). The relevant differential thermogravimetry (DTG) curves were processed as well in order to display the decomposition temperature (T_d). In addition, differential scanning calorimetry (DSC, Q100, TA instrument, Castle, DE) was used to determine the thermal phase transitions of the lignins and the films. The samples were loaded in a hermetic aluminum pan under nitrogen flow rate of 50 ml/min. The samples were isothermally kept at 105 ^{o}C and a heating cycle was started from 40 ^{o}C to 300 ^{o}C. DSC plots of heat flow (W/g) versus temperature were obtained.

Film strength. The tensile strength of the films were tested by a dynamic mechanical analyzer (DMA, Q800, TA instrument, Castle, DE) equipped with a film tension strength clamp. The tests were conducted under controlled force mode with an initial load of 0.1N. The stress was raised from 0 to 50 MPa using 2 MPa/min at room temperature. Stress-strain data was collected until reaching film fracture.

Film morphology. A variable pressure scanning electron microscopy (SEM, Hitachi S3200N, Tokyo, Japan) was used to examine the morphology of the PAN-Lignin films. First, the film samples were dried overnight in an oven at 60^{o}C. Following, the films were cut into slides and immersed in liquid nitrogen. Cyro-fractured films were obtained and coated with gold under nitrogen atmosphere and film cross-section images were obtained at different magnifications.

RESULTS AND DISCUSSION

Production and Characterization of Vinyl Silylated Lignin.

Reactive extrusion. As a thermal set material, it is very difficult to process kraft lignin under melting extrusion. Crosslinking and thermal degradation easily occurs when lignin is heated up to its melt temperature. Moreover, the crosslinking or thermal degradation occurs within a short resistance, which limits lignin mobility.[38] As a compromise, a fractionation process or plasticizer addition is required to extrude lignin successfully.[28, 47]

We use the high shear rate of reactive extrusion to facilitate mixing for the vinyl silylation reaction to occur and to minimize the overall cycle time to the order of minutes, without the need for additional solvent. The flow process of reactive extrusion of ViSiL is shown in Figure 1. The lignin and DVDZ were premixed under N_2 flow before injecting into the twin-screw extruder. With appropriate ratio of lignin and DVDZ, the vinyl silylation reaction occurred under higher temperature and pressure compared with the bench-top solution reaction. DVDZ reacted with the -OH group of the kraft lignin, which limited lignin crosslinking at high temperature. Moreover, DVDZ performed similar function as a plasticizer to extrude the modified lignin easily. After drying and grinding, the ViSiL was used for copolymerization.

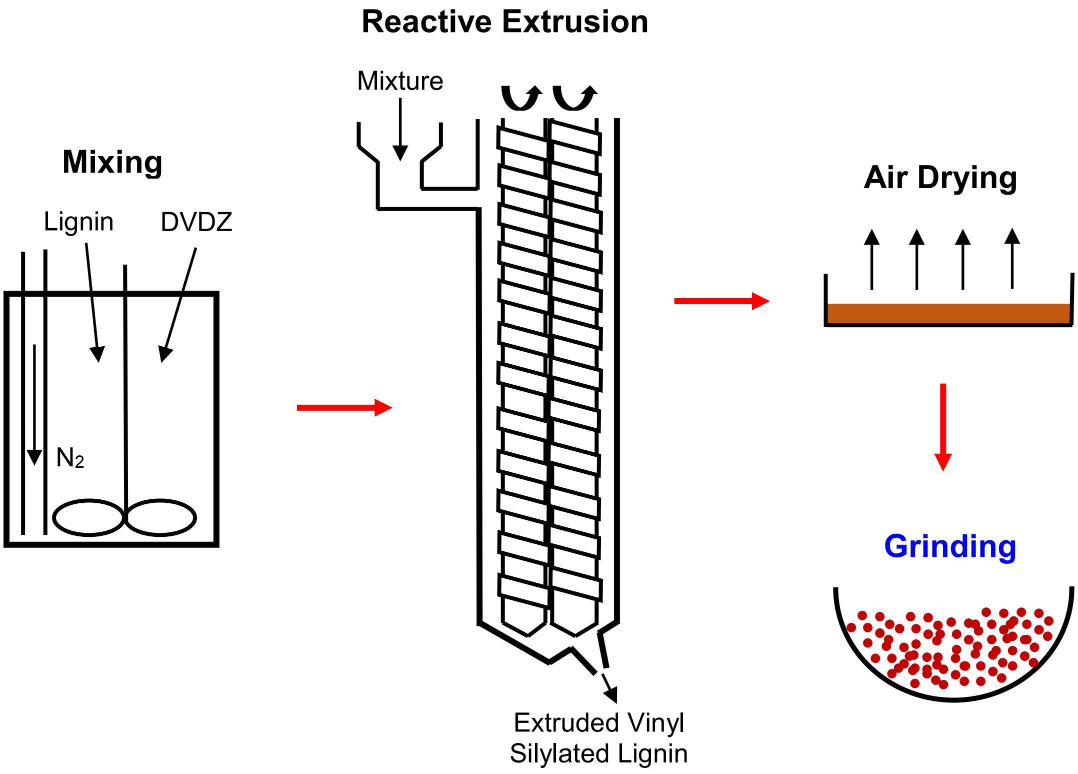


Figure 1. Flow process of reactive extrusion of vinyl silylation of lignin

FT-IR analysis. FT-IR spectra of KL and ViSiL are shown in Figure 2. The absorption at 3055 cm^{-1} corresponds to the *sp*^{2} C-H stretch, which together with the peaks observed at 1592 cm^{-1} and 1407 cm^{-1} indicated the presence of $Si\text{-}CH{=}CH_2$ units. We note that the peak at 1592 cm^{-1} is also characteristic of other alkenyl groups that might exist in lignin. Si-CH=CH_2 was further identified by NMR analysis. A sharp and strong peak at 1251 cm^{-1} indicated the contribution of C-H stretch connected with silicone (Si-CH_3 groups). Moreover, the strong absorbance at 835 cm^{-1} and 785 cm^{-1} is characteristic of Si-CH_3. The Si-O-C signal was observed as an absorption signal at 1008 cm^{-1}. The Si-O-Ph group presented a strong peak at around 1240 cm^{-1}. Although, this peak may overlap with that at 1251 cm^{-1}, the signal at 957 cm^{-1} further supports the presence of Si-O-Ph groups. Overall, the FT-IR analysis confirmed the presence of Si-O-C and Si-CH_3 groups. Other groups were identified further by NMR analyses, as presented in next section.

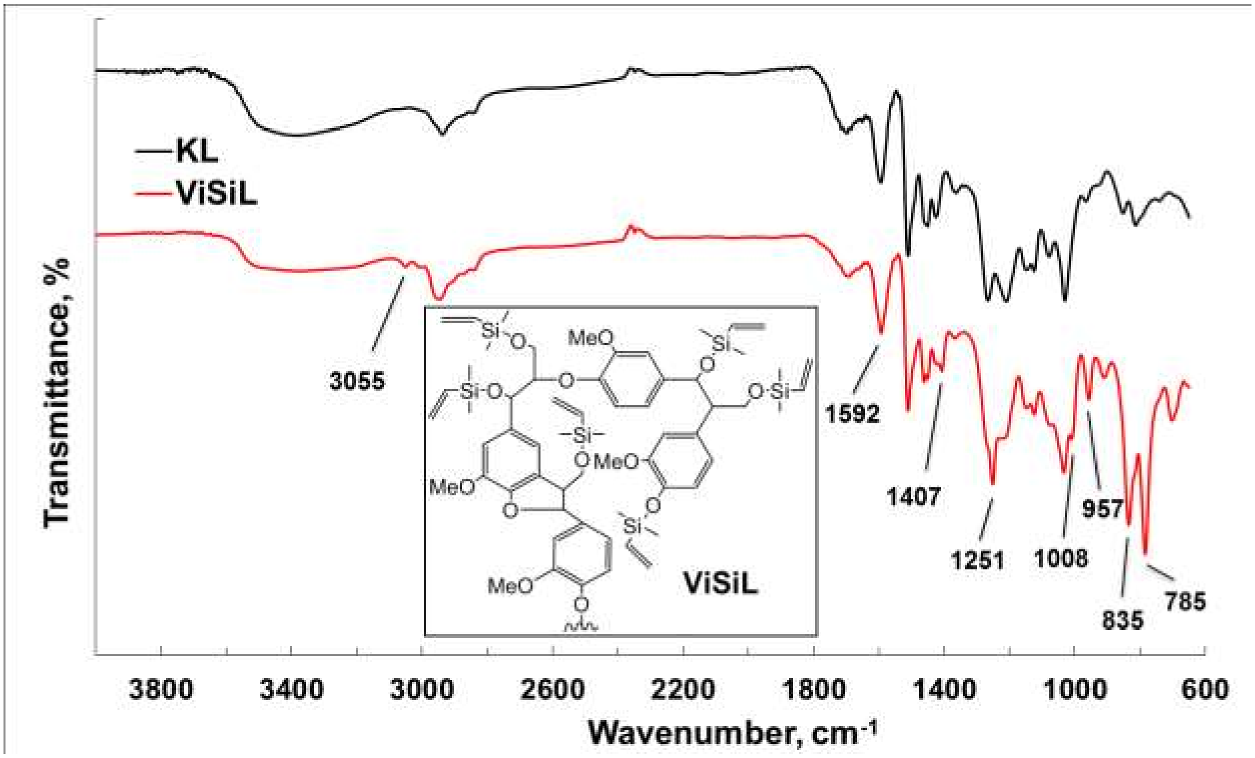


Figure 2. FT-IR spectra of kraft lignin (KL) and vinyl silylated lignin (ViSiL)

^{31}P NMR analysis. ^{31}P NMR spectra (Figure 3) indicated that the amount of hydroxyl groups of the vinyl silylated lignin were reduced relative to that of the kraft lignin. In addition, both, aliphatic hydroxyl groups, with peaks between δ_P (150-145) ppm, and phenolic hydroxyl groups, within the

δ_P range of 145-137 ppm, were reduced. This was taken as indication that the vinyl silylation was not selective for the hydroxyl groups. According to the internal standard, the total hydroxyl groups was calculated to be ~8 mmol/g and the substituted hydroxyl groups can be calculated to be ~2.5 mmol/g corresponding to the silicone and vinyl groups that were introduced in the modified lignin. Accordingly, the degree of substitution was calculated to be ~31 %.[27]

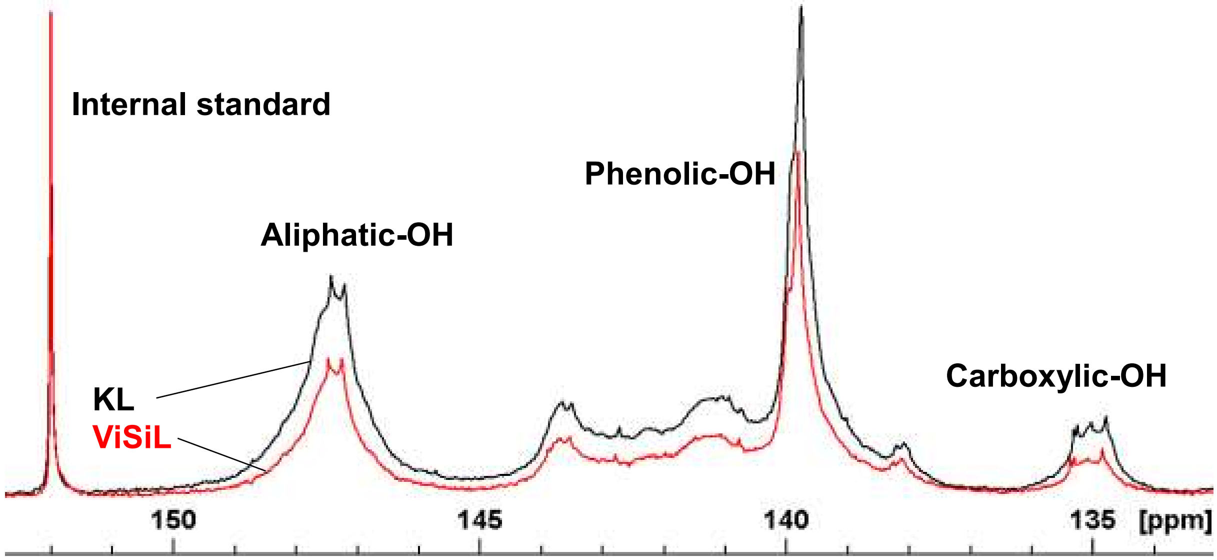
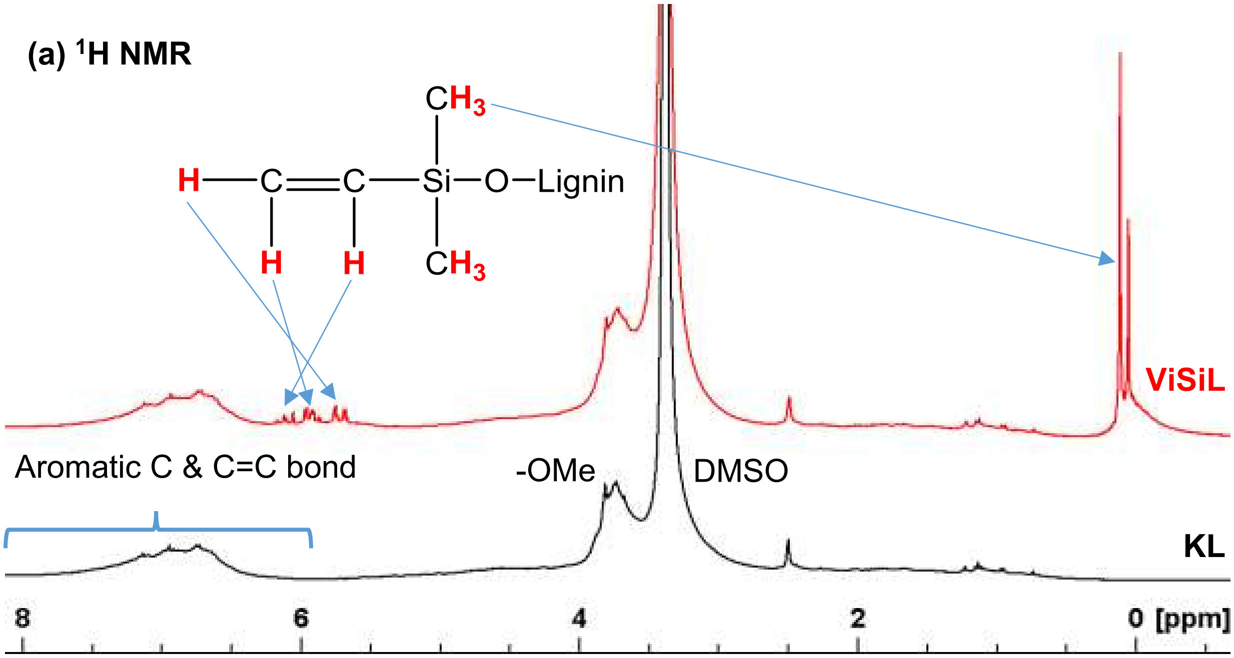


Figure 3. Quantitative ^{31}P NMR spectra of kraft lignin (KL) and vinyl silylated lignin (ViSiL).

NMR analysis of lignins. ^{1}H NMR spectrum of KL displayed two major wide peaks (Figure 4a). The region of δ_H (6.0 - 8.0) ppm indicated aromatic protons. The methylene and methoxyl protons were assigned to the δ_H region (2.8 - 4.2) ppm. This observation is in good agreement to a kraft lignin reference.[26, 45] The functionalized ViSiL maintained the major structure of the kraft lignin but presented a strong peak at around $\delta_H = 0$ ppm, which was assigned to silyl protons. Moreover, at about $\delta_H = 6.1$ ppm, a triplet peak indicated the existence of alkene protons in =CH- groups. The complex multiplet peaks around the region δ_H (5.7-6.0) ppm can be assigned to the alkene protons in =CH_2 groups.[48] Together with the results from FT-IR (Figure 2), there is indication of the successful modification of lignin via the vinyl silylation reaction (Scheme 1).

The ^{13}C NMR spectra (Figure 4b) were collected to further verify the vinyl silylation of lignin. Compared with the kraft lignin, a newly formed singlet peak at $\delta_C = 0$ ppm indicated the silyl carbon. The triplet peak at δ_C 131 ppm can be assigned to the =CH_2 group. A doublet peak appeared at δ_C 140 ppm, which corresponds to the =CH- group.[49] The results showed a good agreement with the ^{1}H NMR spectra included in Figure 4a. Together, they confirm the modification carried out with the kraft lignin.



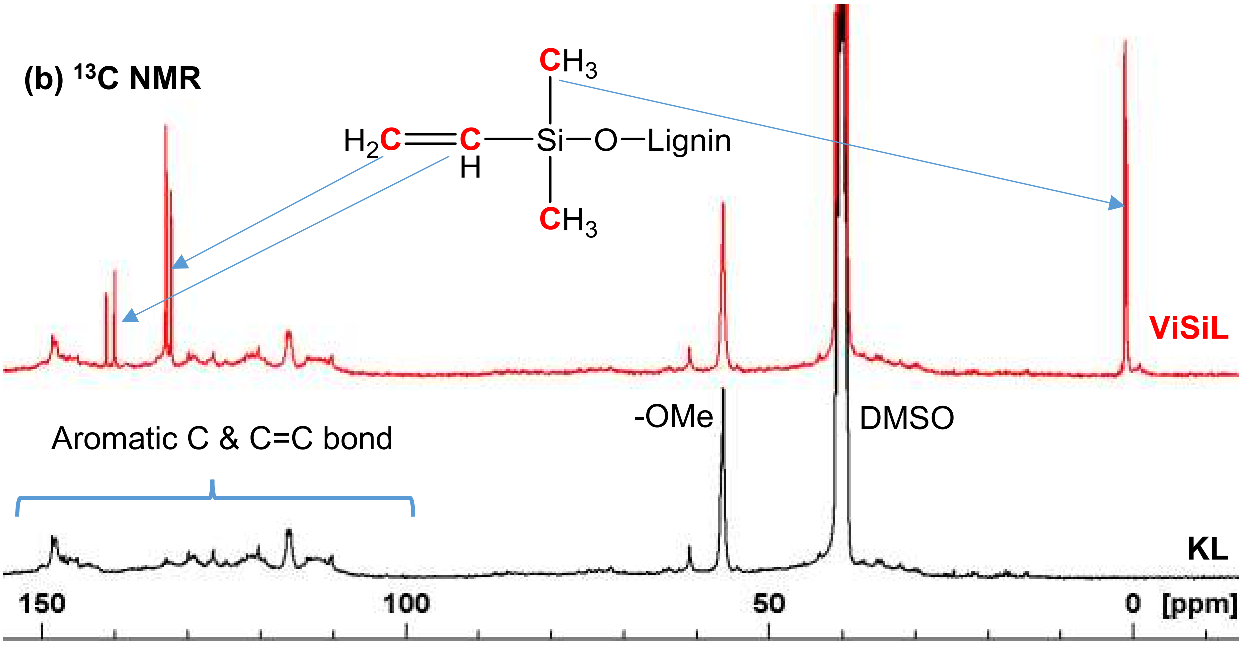
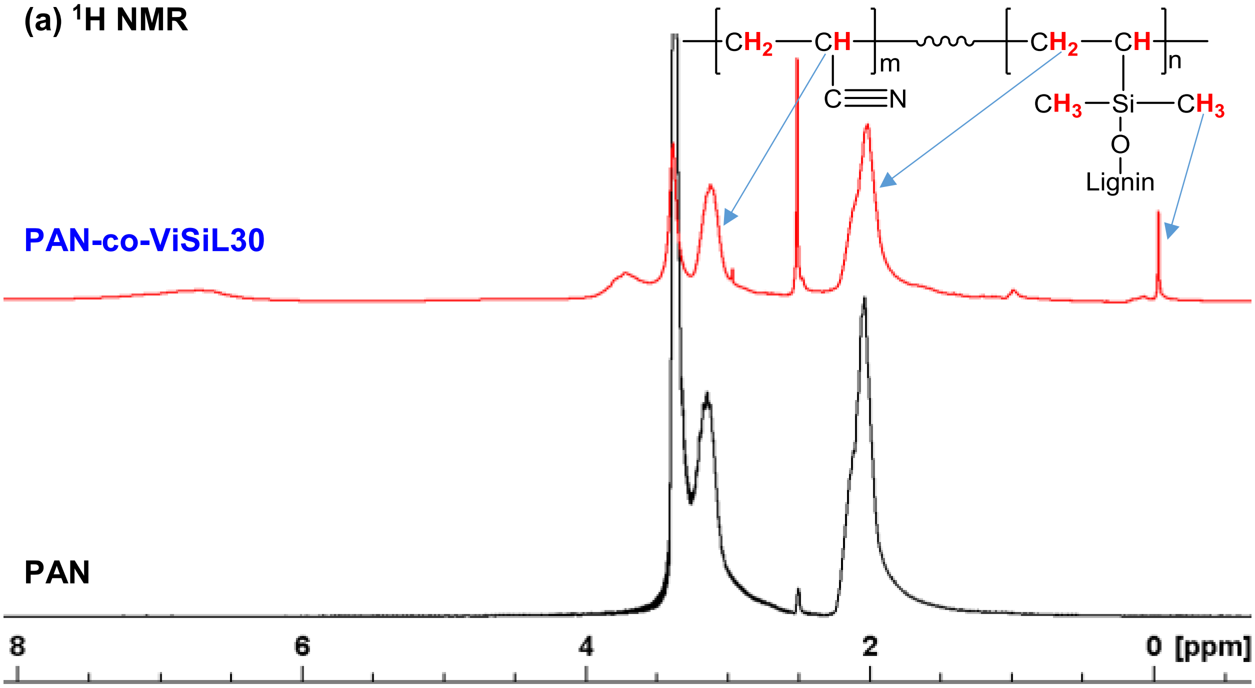


Figure 4. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of kraft lignin (KL) and vinyl silylated lignins (ViSiL).



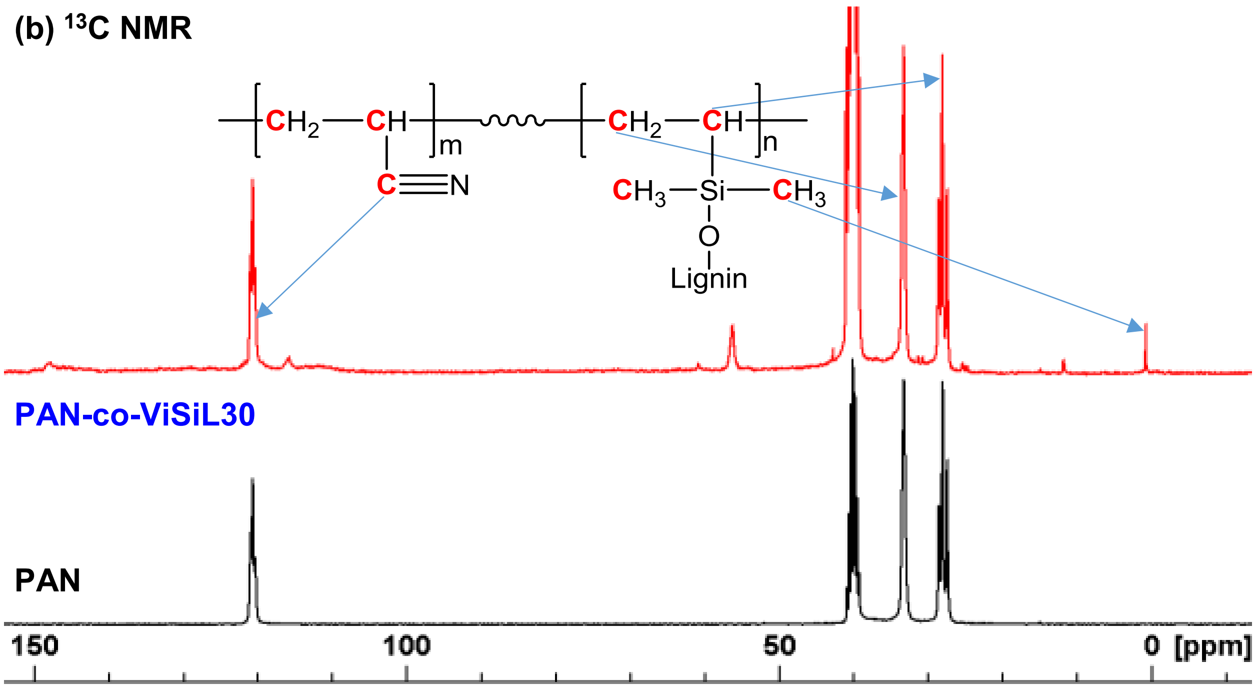


Figure 5. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of PAN and PAN-co-ViSiL30 copolymer.

NMR analysis of the copolymer. The PAN ^{1}H NMR spectrum (Figure 5a) showed two singlet peaks indicating the secondary proton at δ_H = 2.0 ppm and the tertiary proton at δ_H = 3.1 ppm which is in agreement with the reference. [50] After copolymerization the ^{1}H NMR spectrum of the resultant PAN-co-ViSiL30 presented all the characteristic peaks of both PAN and ViSiL except the alkene protons. This is an indication of the free radicals polymerization based on the unsaturated vinyl groups, which were catalyzed by hydrogen peroxide. The activated double bonds in ViSiL copolymerized with the acrylonitrile oligomeric chains to form PAN-co-ViSiL30 copolymer.

The ^{13}C NMR spectrum of PAN (Figure 5b) displayed the signal at δ_C = 120 ppm, which was assigned to the nitrile group. The other secondary and tertiary carbons were observed at δ_C = 33 and δ_C =28 ppm, respectively.[51] After the copolymerization to yield PAN-co-ViSiL30, and similar to ^{1}H NMR, the ^{13}C NMR spectrum maintained all the characteristic signals of ViSiL and PAN except the alkene carbons. All above spectra provided evidence of successful modification of lignin into ViSiL as well as its copolymerization with PAN.

PAN-Lignin films

Rheology. The rheological behavior of the PAN-co-ViSiL copolymers with different AN:ViSiL ratios are displayed as plots of viscosity as function of shear rates from 1-1000 s^{-1} (Figure 6a). The PAN-co-ViSiL casting solutions presented a Newtonian behavior at low shear rates but became shear thinning at shear rates > 10 s^{-1}. A reduction in apparent viscosity was noted with the increase in ViSiL fraction in the copolymer, from 0 (neat PAN) to 30 %. The viscosity at shear rate of 1 s^{-1} for PAN-co-ViSiL30 was around 2.2 Pa·s, which is much smaller than that of PAN (22.1 Pa·s). According to quantitative ^{31}P NMR analysis (Figure 3), 31 % of hydroxyl groups of kraft lignin were replaced with same vinyl group molar content. On the basis of hydroxyl group content of 8 mmol/g in kraft lignin, around 2.5 mmol/g of vinyl groups can be calculated to exist in ViSiL. Since the molecular weight of ViSiL was over 6000 Da, it can be calculated that each ViSiL molecule contained 15 vinyl groups, approximately.

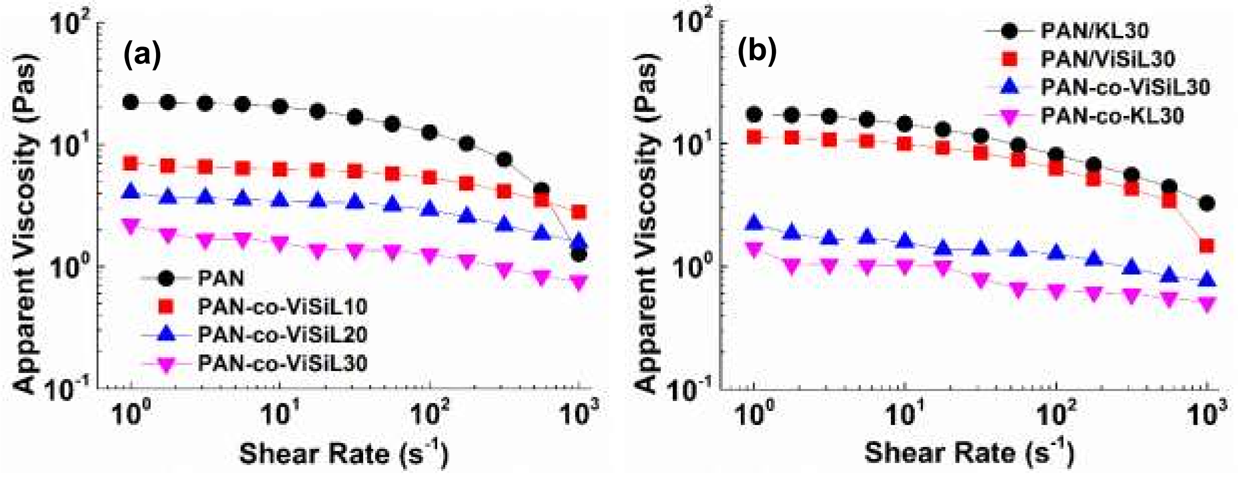


Figure 6. Flow curves of casting solutions (in DMSO solvent) of (a) PAN and PAN-co-ViSiL copolymers with varying AN/ViSiL ratio, as noted. Included are also the profiles for (b) PAN-

lignin copolymers (PAN-co-ViSiL30 and PAN-co-KL30) and PAN/lignin blends (PAN/KL30 and PAN/ViSiL30).

The synthesized PAN was analyzed and compared with the commercial PAN (Mw = 150,000 Da, Sigma-Aldrich, St. Louis, MO), which displayed similar rheological behavior. It can be assumed that the molecular weight of the PAN used in our experiments was of the same order of magnitude. The theoretical alkene groups from acrylonitrile are 43.9 mmol/g for each vinyl group in ViSiL, 18 acrylonitrile molecules are present in the PAN-co-ViSiL30 copolymer. Therefore, the pure acrylonitrile polymerization formed very long linear chains with a degree of polymerization >2000. However, ViSiL is expected to be a branched macromolecule, i.e., when the lignin units connected with PAN, a branched copolymer is formed. Additionally, the polydispersity of lignin make the detailed description of the copolymer system quite complex and beyond the scope of this report. The degree of polymerization of PAN-co-ViSiL copolymer could not reach values as high as those of the neat PAN. PAN-co-ViSiL copolymers displayed lower apparent viscosity than PAN, in agreement with the expectation from the correlation between degree of polymerization and viscosity. On the other hand, the PAN solution showed a sharp decline in viscosity at high shear rates (strong shear thinning behavior). This is because long PAN chains entangle in solution forming strong networks via intermolecular van der Waals forces, which are disrupted and become aligned under flow fields. The PAN-co-ViSiL copolymers are branched structures that are affected by shear to a limited extent.

The apparent viscosity changes of the PAN/lignin blends and PAN-lignin copolymers with 30% of KL or ViSiL are shown in Figure 6b. For both lignins (KL and ViSiL), their blends with PAN presented higher viscosity than their copolymerized products (PAN-co-KL30 and PAN-co-ViSiL30). PAN, with a high molecular weight, played a leading role in the behavior of the blend, displaying a relatively high apparent viscosity if compared with the copolymerized products (with a relatively lower molecular weight). Thus, a sharp viscosity reduction at high shear rate occurs, as was discussed above.

The PAN/ViSiL30 blend solution presented a lower apparent viscosity than that of PAN/KL30 blend solution. This can be explained by the fact that ViSiL has a better solubility in the organic solvent, which enhanced chain mobility and reduced the apparent viscosity under shear. However, compared to PAN-co-KL30 copolymer, the PAN-co-ViSiL30 copolymer solution presented a higher apparent viscosity. This is because the large amount of vinyl groups in ViSiL and thus the high reactivity with acrylonitrile oligomers during copolymerization. Therefore, the PAN-co-ViSiL30 copolymer product, a multi-branched macromolecule, contained, on a relative basis, stronger chemical bonds/connections and had a higher molecular weight, resulting in a higher viscosity.

Thermal properties. The thermal degradation behavior of the lignins, PAN, and PAN-lignin copolymers were tested by TGA and DTG analyses. PAN presented a rapid weight loss at 284 ^{o}C which indicated a fast degradation due to breaking of the long chain to oligomers (Figure 7a). At this stage, small molecules, such as CH_4, NH_3 and HCN are released.[52] Not like typical polymers, kraft lignin showed an onset of weight loss at temperature > 100 ^{o}C but the major decomposition occurred at ~220 ^{o}C. Total decomposition occurred in a wide temperature range, a result of the complexity of lignin biomacromolecules. The components in lignin have a molecular weight ranging from 1,000 to over 10,000 and carry different functional groups that result in a large range of degradation temperature. After vinyl silylation, the ViSiL displayed two major degradation temperatures. The first one, at higher temperature compared with the kraft lignin, shows a ~6 % weight loss at 153 ^{o}C (Figure 7a and 7c). This can be ascribed to the partial breaking of Si-O-C bonds. Compared to the Si-O bond, C-O bonds are relatively longer (143 pm) and have lower bond energy (358 KJ/mol).[53] Therefore, the C-O bonds in lignin were more easily broken to form small fragments. Based on the 2.5 mmol/g content of functional groups (Mw~85 Da) in ViSiL, it could be roughly calculated that ~28 % (0.7 mmol/g) vinyl silylated groups were lost from ViSiL. The second degradation step occurred at a decomposition temperature of 226 °C, similar to that of KL.

When ViSiL was copolymerized with acrylonitrile, the decomposition shifted to higher temperatures, approaching that of the degradation of PAN. During copolymerization, the vinyl groups were polymerized or cross-linked with the neighboring active double bonds. Even though a small part of the C-O bond were broken, the molecules were not able to volatize from this network and therefore no major weight loss was recorded (according to the DTG profiles in Figures 7c and 7d, the PAN-co-ViSiL30 copolymer did not show any apparent degradation below 265 °C).

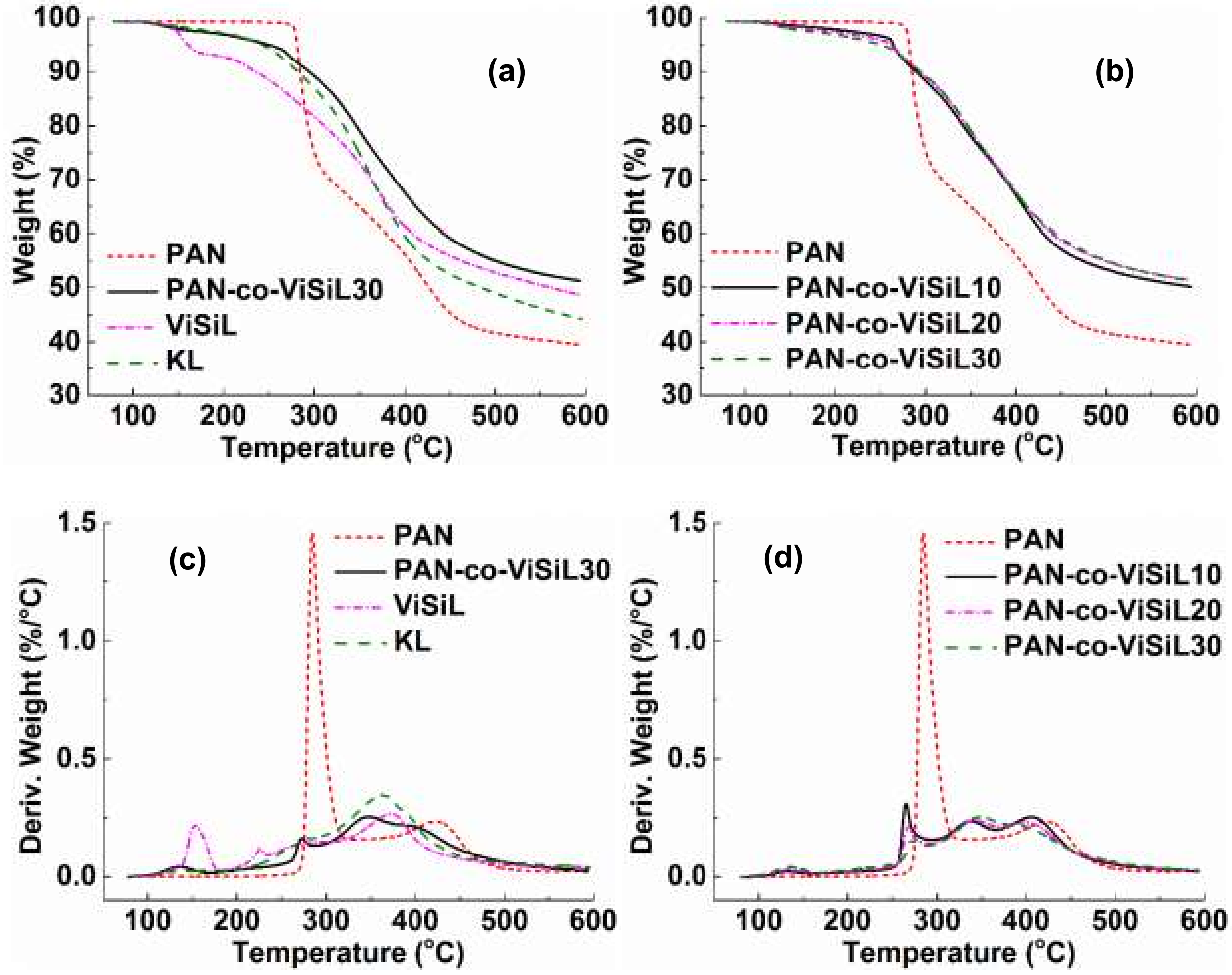


Figure 7. (a) Thermograms (TGA) for (a) PAN, KL, ViSiL and PAN-co-ViSiL30 copolymers and (b) PAN-co-ViSiL copolymer films of varying AN/ViSiL ratio. (c) and (d) includes the differential thermogravimetry (DTG) profiles for the respective polymers in (a) and (b).

PAN-co-ViSiL films with varying AN/ViSiL ratios were also investigated (Figure 7b). The PAN-co-ViSiL films displayed PAN-like thermal character with apparent decomposition temperature around 270 °C (Figure 7d), also comparable to that of ViSiL or KL. However, the PAN-co-ViSiL films presented around 5 % weight loss, a contribution from the lignin component. Apparently, with higher ViSiL concentration, the weight loss is larger in the low end of the decomposition range. However, the decomposition temperatures slightly increased with the ViSiL addition in the copolymers, as shown in Figure 7d and Table 1. Generally, the PAN-co-ViSiL films did not present the fast decomposition characteristic of PAN films. The molecular weight of PAN-co-ViSiL copolymers were much lower than PAN; therefore, even for PAN content as high as 90 %, the molecules were not degraded to smaller sizes as rapidly as in the case of neat PAN films. Additionally, due to the effect of the lignins, PAN-co-ViSiL films presented a residual 50 % mass at 600 °C while for the PAN film it was less than 40 %.

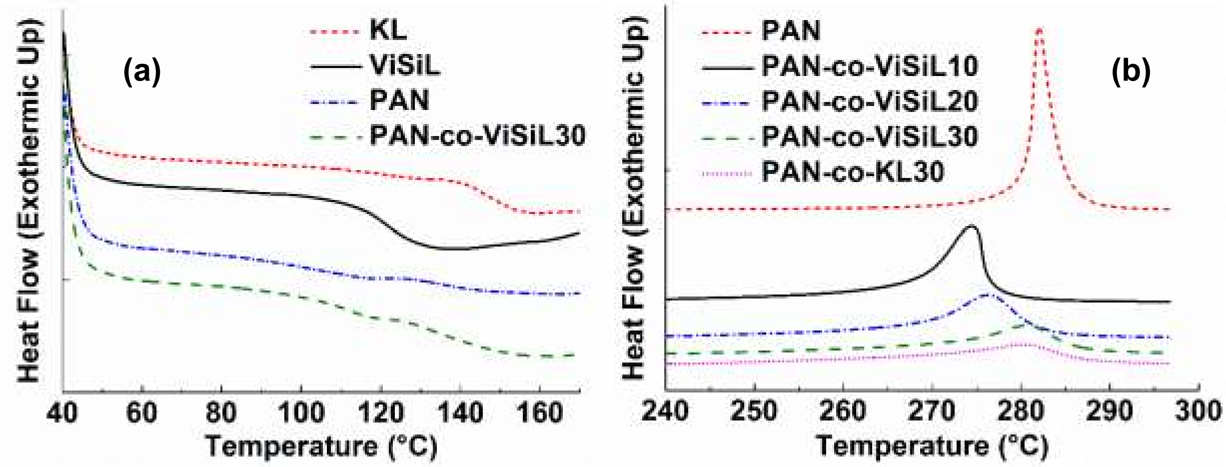


Figure 8. Differential scanning calorimetry (DSC) analysis of (a) lignins (KL and ViSiL) as well as PAN and PAN-co-ViSiL30 copolymer films. Thermograms at the high temperature range is included in (b) for PAN, PAN-co-ViSiL copolymers with varying AN/ViSiL ratios, and PAN-co-KL30.

The glass transition behaviors of the lignins and the films were monitored by DSC (Figure 8). The kraft lignin used in this work, an amorphous biopolymer, presented a glass transition temperature (T_g) of 145°C, as shown in Figure 8a. After vinyl silylation, the ViSiL presented a lower T_g of 121°C. This can be explained by the fact that silicone-containing materials present an inherent higher molecular mobility. Compared with carbon, silicon usually forms longer bonds, with wider bond angle that make silicone-based chemical bonds more free to rotate. Moreover, the double bonds are typical flexible groups. Thus, it is not surprising that ViSiL, rich in Si and alkene, displayed a lower glass transition temperature compared to KL.

As a unique semi-crystalline polymer, it has been shown that unoriented PAN presents two glass transition temperatures, corresponding to laterally-ordered and amorphous domains.[54] Good agreement with the expectation for PAN is indicted in Figure 8a: a first glass transition temperature (T_{g1}) took place at ~ 102 ^{o}C. Not like typical glass-rubber transition, at this temperature, the transform was from a laterally-ordered glassy state to a more mobile but still laterally ordered state. The second T_{g2} appeared at ~136^{o}C, which is ascribed to the transformation into an amorphous structure. Each C9 unit of the kraft lignin only has one reactive site for polymerization. Thus, the kraft lignin was copolymerized with AN oligomers but did not contribute with chain growth. In contrast, the coupling between AN oligomers and the active sites in KL more likely terminated the polymerization and resulted in a lower molecular weight, as discussed in Figure 6b. However, in the case of ViSiL the copolymerization can be extended due to the open double bonds. Thus, as shown in Figure 8a and Table 1, the PAN-co-ViSiL30 copolymer displayed clearly two glass transition temperatures.

Table 1. Glass transition (T_g), melting (T_m) and decomposition (T_d) temperatures for the kraft lignin, PAN and copolymers

Material	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)	T_d (°C)
KL	N/A	145	N/A	220
ViSiL	N/A	121	N/A	226
PAN	102	136	282	284
PAN-co-ViSiL10	108	133	274	265
PAN-co-ViSiL20	109	132	276	268
PAN-co-ViSiL30	112	131	280	272
PAN-co-KL30	110	132	280	273

With the increase in ViSiL ratio in the copolymer film, the first T_g shifted from the 102 °C typical of PAN to 112 °C (Table 1). The second T_g, indicating the contribution of the amorphous structures, was reduced from 136 °C in PAN to 131 °C in PAN-co-ViSiL30. Considering the T_g of ViSiL (121 °C), the glass transition temperatures of the copolymers were shifted to intermediate values between those of the two polymers, which indicates a good polymerization reactivity in the copolymer.

In addition, the DSC curves of PAN and PAN-lignin copolymers indicated the thermal stabilization process of PAN-based materials (Figure 8b). A sharp peak representing PAN film in the DSC curve, at 282 °C, was revealed, which was similar to T_d =284 °C (Table 1). This indicated an exothermic reaction, attributed to cyano cyclization and dehydrogenation. It is also shown that PAN-co-ViSiL copolymers (PAN-co-ViSiL films) presented a less intense exothermic reaction. This could be explained by the fact that ViSiL oligomers can block the cyclization if they are copolymerized as a block segment in the long chains of the copolymer. Thus, the cyclization reaction involved small segments compared with the PAN homopolymer. Therefore, the intensity of the exothermic reaction was reduced with the increased ViSiL/AN ratio. However, compared to the PAN-co-KL30 copolymer, the PAN-co-ViSiL30 displayed a higher intensity. This is taken as additional evidence that KL blocks chain growth of PAN and terminated the polymerization, limiting the degree of cyclization. Moreover, compared with PAN, the PAN-co-ViSiL10, PAN-co-ViSiL20 and PAN-co-ViSiL30 copolymers displayed lower cyclization temperatures, i.e., 274, 276, and 280 °C, respectively. As shown in Table 1, the decomposition temperatures of the PAN-co-ViSiL copolymers displayed close values and same observed trend with increased ViSiL concentration. Pyrolysis of ViSiL at high temperature could form small oligomers, gas molecules, segments of aromatic rings, etc. These groups could accelerate the dehydrogenation and cyclization reaction of PAN and lower the reaction temperature. However, with ViSiL, the PAN-co-ViSiL copolymers formed a stronger network that required more energy to decompose. Thus, the thermal stabilization required higher temperatures with increased ViSiL content.

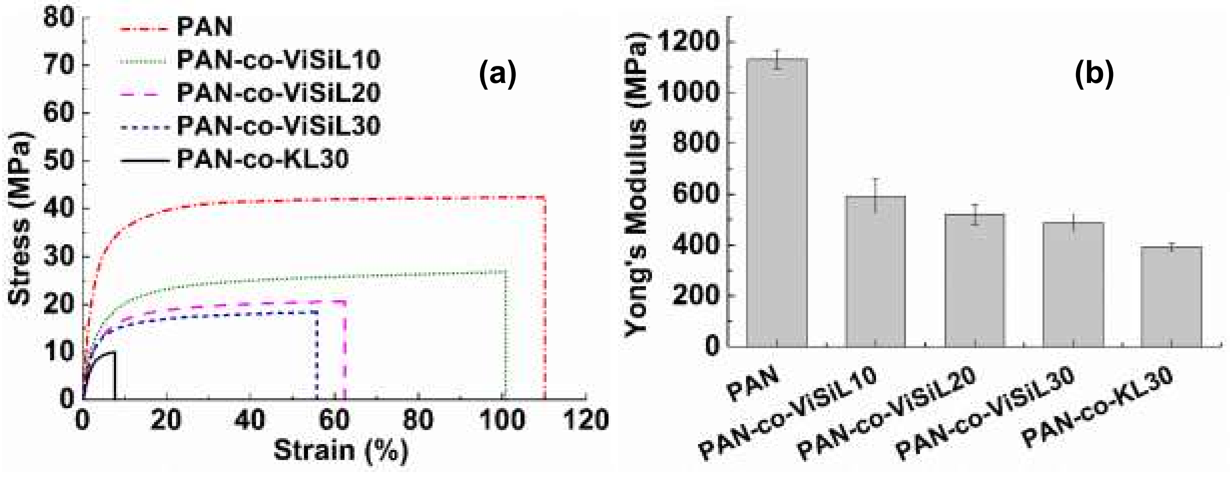


Figure 9. Tensile strength (a) and Young’s Modulus (b) of films produced from PAN, PAN-co-KL30 and PAN-co-ViSiL copolymers with varying AN/ViSiL ratio.

Film strength. The tensile strength as function of strain is shown in Figure 9 to describe the mechanical performance of the films. The PAN film presented a very high yield stress, around 30

MPa and an ultimate stress over 40 MPa. At the fracture point, the PAN film strain reached values as high as 110 %. As expected, with the increased ViSiL content in the PAN-co-ViSiL copolymers, the films presented a lower stress and strain. For PAN-co-ViSiL30 copolymer film, the ultimate stress was reduced to 18 MPa and the strain was 55 % at the fracture point. As discussed in the rheology section, the PAN-co-ViSiL copolymers has a lower degree of polymerization compared to that of neat PAN. Amorphous lignin segments weakened the PAN chains to form laterally-ordered phases and made the film relatively brittle. However, the PAN-co-ViSiL30 copolymer displayed much better performance than the PAN-co-KL30 copolymer. The PAN-co-KL30 copolymer film displayed an ultimate stress of less than 10 MPa. Compared to PAN-co-ViSiL30, the flexibility of PAN-co-KL30 copolymer was very limited, a strain of 10 % at the failure point was measured.

The Young's modulus of PAN films reached 1 GPa, while PAN-co-ViSiL copolymers displayed around half this values and became smaller with ViSiL loading. For PAN-co-ViSiL30 copolymer film, the Young's modulus was 486 MPa, higher than that for PAN-co-KL30 film of 394 MPa. Two major reasons can explain the latter observations: 1) ViSiL presented good polymerization reactivity as a copolymer with PAN, undergoing chain growth due to the open double bonds and, 2) the silicone-containing ViSiL is more flexible due to the bond length and wide bond angle of Si-O and Si-C. Thus, the PAN-co-ViSiL30 copolymer was not brittle as was the case of PAN-co-KL30 copolymer. The results indicate that the PAN-co-ViSiL30 copolymer formed a more connected network compared to the PAN-co-KL30 copolymer sample that likely contained lignin radicals causing polymer termination.

Film morphology. There were not significant differences in the morphology of the copolymer films. This can be explained by the slow evaporation of DMSO in the oven during the process of film preparation. The copolymers dispersed very well in the organic solvent that in turn improved their uniformity. Thus, the SEM images of the films are not discussed here but included in the supporting information. Instead, the morphology of the PAN-lignin hot-pressed copolymer films were observed by SEM imaging in order to assess polymers phase compatibility (Figure 10). The cryo-cross section of neat PAN film presented a smooth rupture surface. The PAN-co-KL30 copolymer hot-pressed film displayed a much rougher surface. It was observed that, within the red circle of the image (Figure 10e), a number of small holes were detected. In contrast to this latter case, the PAN-co-ViSiL30 hot-pressed film (Figure 10f) displayed a continuous and uniform surface with limited "breaking points".

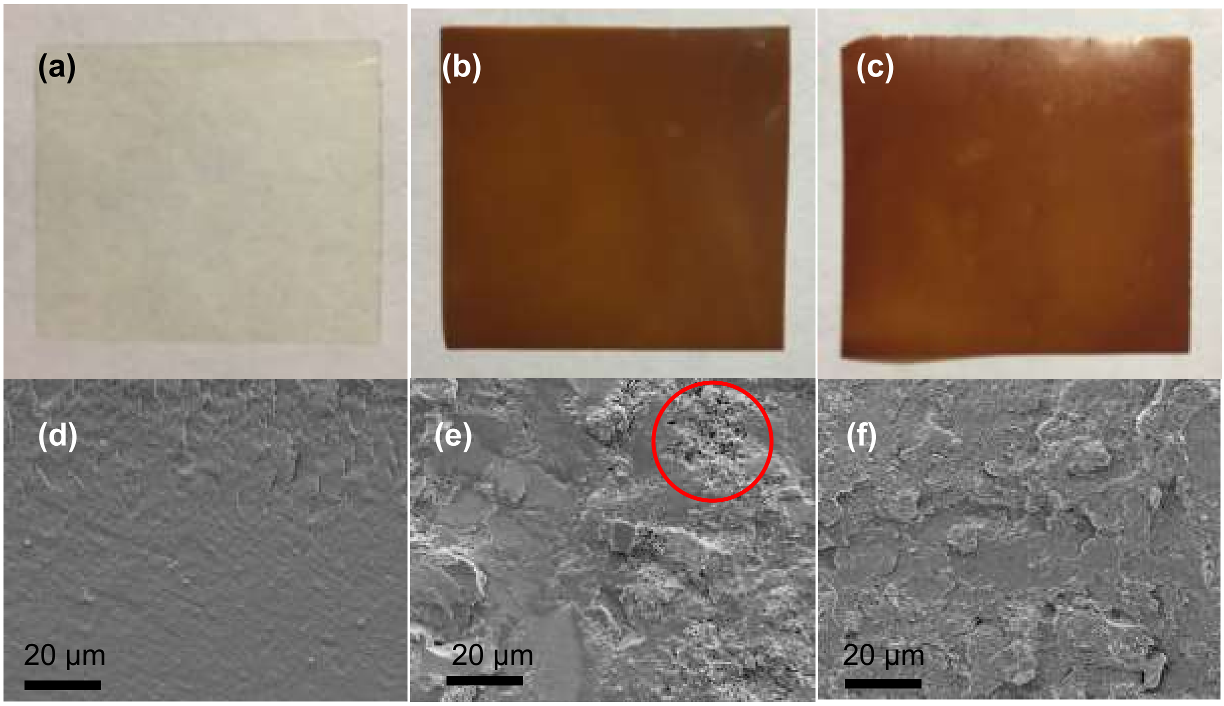


Figure 10. Optical images of (a) PAN, (b) PAN-co-KL30 and (c) PAN-co-ViSiL30 films (2.5cm x 2.5cm). Cross section SEM images (1000x) of (d) PAN, (e) PAN-co-KL30 and (f) PAN-co-ViSiL30 hot-pressed films.

PAN is a highly homogeneous polymer which presented highly homogeneity on the cross surface. However, due to the less reaction sites of kraft lignin, the copolymerization reactivity between PAN and kraft lignin was very limited. The final product displayed a more complex but more loosen structure with large lignin molecules as the terminal group of the PAN chains. Additionally, the low reactivity between PAN and KL resulted in a relative low purity product, containing possible unreacted lignin molecules. Therefore, with the short melting period, not like the highly purified PAN, the PAN-co-KL30 hot-pressed film presented discontinuous phase on the cross section. Although PAN-co-ViSiL30 hot-pressed film displayed a rougher cross section surface than PAN. ViSiL is much more reactive than KL because of the large amount of vinyl groups that copolymerize with PAN to form a much stronger network connection. Therefore, the PAN-co-ViSiL30 hot-pressed film displayed better homogeneity than PAN-co-KL30 film. Finally, the films obtained here were used in the synthesis of membranes and carbonized films, demonstrating additional potential applications. This is a subject of an upcoming publication.

CONCLUSIONS

A vinyl silylation reaction carried out in a reactive extruder was successfully applied to a kraft lignin to yield a degree of substitution of 31%. The obtained vinyl silylated lignin was copolymerized with AN oligomers to form a copolymer. The respective systems were casted taking advantage of the relatively low viscosity endowed by ViSiL loading. Compared with the copolymers from the unmodified kraft lignin (PAN-co-KL30), the PAN-co-ViSiL30 copolymer presented a higher molecular weight due to a higher reactivity, which in turn resulted in a higher viscosity. The TGA profiles indicated that the copolymerization improved the thermal stability of ViSiL. The weight loss of the copolymer was reduced with the increased AN/ViSiL ratio. In addition, DSC analysis indicated a relatively low T_g for ViSiL due to the silicone-containing structures, which improved the flexibility of the macromolecule. The copolymers displayed a T_g

that was intermediate to the values of the precursor polymers, which indicated successful copolymerization. Moreover, the ViSiL increased the thermal stabilization in PAN-co-ViSiL copolymers but decreased with the ViSiL/AN ratio, due to strong network formation. In addition, the tensile strength of the PAN-co-ViSiL copolymer films showed lower strength and strain at fracture with increased ViSiL/AN ratio. However, compared with the PAN-co-KL30 film, the PAN-co-ViSiL30 displayed a much higher tensile strength and strain (18 MPa and 55% strain) indicating the flexibility of the PAN-co-ViSiL copolymers. Finally, PAN-co-ViSiL30 cohesion was better compared to that of PAN-co-KL30, indicating the higher polymerization reactivity. In sum, due to its cohesion, flexibility and high reactivity during co-polymerization, PAN-co-ViSiL copolymers can be expected as a suitable precursor for membranes or carbon films.

ASSOCIATED CONTENT

Supporting Information

Cross section SEM images of films are available as supporting information in the web.

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TABLE OF CONTENTS GRAPHICS (TOC)

Synopsis: Lignin, a low-cost and sustainable biopolymer, is efficiently modified through vinyl silylation in a continuos reactive extruder, aming to partially replace high-cost PAN and increase flexibility of the copolymer in films.

For Table of Contents Use Only