

# Strategies towards Novel Carbon Fiber Precursors: the Research Results on the Synthesis of PAN Copolymers via AGET ATRP and on Lignin as a Precursor

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## Abstract

The aim of this work is the presentation of two different approximations for improving the production of carbon fibers through the introduction of alternative precursors. The first approach concerns the development of novel polyacrylonitrile block copolymers through activators' generated by electron transfer-atom transfer radical polymerization (AGET-ATRP) reaction mechanism in microemulsion; the novel polymers are envisaged to contain a structure that will be more efficiently oxidatively stabilized and/or carbonized, with the ultimate target of CFs with improved properties. The second approximation aims at the introduction of lignin as efficient CFs precursor; this approach aims at reducing the cost of the process and increasing the production yield. Pyrolysis together with oxidative stabilization of lignin were investigated, as well as the effects on structure and thermal behavior of blending with thermoplastics. Thus far, both these methodologies exhibited significant potential and will be further developed towards full scale industrial application.

## Keywords

Carbon fibers, Lignin, Polyacrylonitrile, Atom transfer radical polymerization

## Introduction

Carbon fibers (CFs) are one of the most important reinforcement materials used for composite manufacturing, as they combine an exceptional set of properties (low density, high stiffness etc.) that makes them ideal for high performance composites; usually CFs are combined with thermo set resin matrices, yet thermoplastic matrix composites have begun to increasingly appear. Even though the industrial scale production of CFs started from the late 1960s/early 1970s, due to several challenges in their manufacturing the production volume has not grown *on par* with the increasing demand; as a result, the price of the CFs-based materials remains still high. Thus, there are still a lot of opportunities for improvement in this field, with the focus being on the precursor material used for carbonization. Currently, the CF precursors of choice are polyacrylonitrile (PAN) and pitch fibers; both of them originate from petroleum and as such they follow its price trends. There are several alternate possible precursors that have been proposed; the most significant is lignin, a natural polymer existing in all plants. Lignin is considered as a sustainable and renewable source, given that large amounts are separated as byproduct from wood during paper pulp production. It is a cross-linked polymer with very high glass transition temperature, and combines aromatic rings substituted by different oxygen-containing groups that are linked together with a combination of ether and carbon bonds. The exact structure of

lignin is not always the same, but it varies depending on the type (and origin) of initial wood, as well as the method used for separating lignin from the wood pulp; depending on the wood used two major categories are recognized: softwood- and hardwood- originating lignin, whereas depending on the wood pulp separation method used there are several categories like Kraft, Organosolv (Alcell, Acetosolv) etc.; however, the vast majority of lignin originates from the Kraft process [1-4].

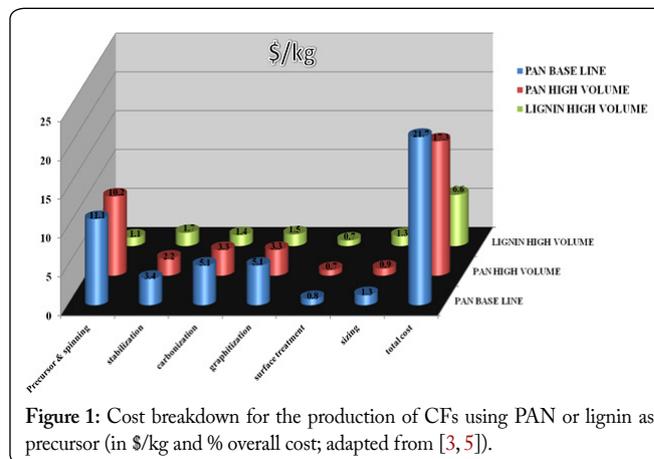
Up to now, CFs composites are mainly applied in aerospace and defense applications, in the blades for wind turbines, as well as high-end sports and leisure items (e.g. bikes, golf clubs). However, the infiltration of CF-based composites in the automotive sector is still limited, with about 5,000 tons per year of CFs used in this sector (out of a total production of 46,500 tons). This is in stark contrast to the fact that it is generally recognized that the use of CF-based composites is the most effective way to reduce the frame weight of the vehicles, which will be the best answer to the problem of improving fuel efficiency and decreasing the greenhouse gas emissions. One of the reasons that the aforementioned proposal has not been yet applied is the high CFs price. Table 1 depicts the mean estimated cost for manufacturing CFs out of different feedstock (actual or proposed) and Figure 1 presents the cost breakdown per each production step [2, 5]. The reference value is the special grade PAN which is currently the dominant precursor material for CF production. The estimated price for melt spun lignin is approximately 1.52 \$ per kg, but it is aimed to be lowered down to 1.1 \$ per kg. This value is much lower than the other precursors such as textile grade PAN (4.4 to 13.2 \$ per kg), melt-spun PAN (6.3 \$ per kg) and polyolefin fibers (1.57 to 2.36 \$ per kg).

**Table 1:** Cost comparison on different carbon fiber precursors [2, 5].

Material	Precursor Cost (US \$/kg)	Production Cost (US \$/kg)	Total Cost (US \$/kg)
Lignin	1.52	6.27	7.79
Polyolefin	1.57-2.36	-	-
Melt-spun PAN	6.3	17.4	23.7
TextileGrade PAN	4.4-13.2	12.25-25.4	16.65-38.6
Special grade PAN	11.1	25.15	36.25

The price estimation for the fibers includes the spinning; in case of PAN, spinning is based on melt assisted or wet spun fiber formation. However, both of these methods are expensive due to the use of solvents (for wet spinning) and the difficulty of obtaining high processing speed (for melt spinning). On the other hand, it is considered that lignin will be efficiently spun into fibers using melt spinning. Taken into consideration that, apart from lignin, the precursors are petroleum based, a possible raise of oil price would further enhance this cost difference [5]. Moreover, the stages of surface treatment and sizing present similar costs and the graphitization step is not

always necessary. Comparing the cost structure between PAN and lignin, the biggest difference arises from the raw material and spinning process, but an additional decrease in the stabilization/ carbonization production line is also expected by the adaptation of lignin.



**Figure 1:** Cost breakdown for the production of CFs using PAN or lignin as precursor (in \$/kg and % overall cost; adapted from [3, 5]).

Thus, it is clear that lignin is probably the optimal precursor for reducing the cost of CF manufacturing. However, there are lots of challenges that have not yet permitted the application of lignin as CFs precursor in large scale. First of all, the most serious problem is that lignin is manufactured as a byproduct, thus the properties of different origins (sometimes, even of different batches from the same production line) may have a wide variation of properties. Currently, there are only a few commercialized (i.e. standardized) lignin products. Given this limitation, it is not surprising that it is not yet clear what type of lignin is the optimum CF precursor. At a second level, due to its chemical structure and intra- and inter-molecular hydrogen bonds, lignin exhibits poor flow properties [6]. It has a very high melting point and the melt spinning of pure lignin is problematic. Right now, lignin is usually co-spun using blends with a more process able polymer (e.g. polyethylene oxide, PEO). Moreover, the phenomena taking place during stabilization are not yet fully understood [2, 5, 7, 8].

High carbonaceous yield (i.e., after proper stabilization) of PAN, is one of the main reasons which constitute this material as the most preferred CFs precursor. Even though the details of the precursors used are a close kept secret from the corresponding producers, it is recognized that fibers used for industrial production are based on PAN copolymer synthesized using conventional free-radical polymerization, most probably using solution (which simplifies the manufacturing process) or suspension techniques; under these conditions it is difficult to control the molecular dimensions and the structure of the synthesized copolymers [9]. Via Controlled/ “living” radical polymerization (CRP) it is possible to tailor the structure of PAN copolymers, thus improving the properties which are essential for a CF precursor candidate. Specifically, ATRP (atom transfer radical polymerization) is a suitable tool for the synthesis of polymers with predefined molecular weights, narrow poly dispersity index and preferred molecular architectures [10]; controlling these polymers’ properties it is possible to produce high performance CFs originated from PAN copolymers. Since the normal ATRP is sensitive to air

and humidity due to low valence transition metal used as catalyst, with the newly AGET (activator generated by electron transfer) ATRP initiation system the limitation of normal ATRP is overcome using a reducing agent. Furthermore, since the synthesis of PAN-based carbon precursor is basically conducted in organic dispersed media, recently the research focuses on more environmentally friendly and more cost-effective synthetic techniques. Aqueous dispersed media are favorable media for industrial scale polymerization, while they are environmentally friendly comparing to the volatile organic solvents. Among various polymerization methods based on aqueous systems, emulsion process is certainly desirable from an industrial perspective, since the method can be directly applicable to current industrial facilities [11].

Currently, further improvement of CFs production relies on advances in several fields, both scientific and technological. Thus, several research paths are explored. As already mentioned, one of the most important topics is the choice of the CF precursors. In that field, the main efforts focus on several directions, however two of them are of particular interest: (1) improving already established precursors [12, 13] and (2) introducing new ones based on sustainable resources [2, 4]. The aim of this work is to present the initial research results on these approximations, namely: (1) synthesis of tailored PAN copolymers by the recently developed technique of AGET-ATRP with microemulsion polymerization and (2) various aspects for the introduction of lignin as a viable CFs precursor.

## Development of Novel PAN-Based Precursors

### Experimental

Acrylonitrile (AN) and methyl methacrylate (MMA) (Sigma-Aldrich) were purified by fractional distillation prior to use. Ascorbic acid (VC) (Serva), hexamethylenetetramine (HMTA) (Fisher Chemical) and Brij 35 (Alfa Aesar), copper bromide ( $\text{CuBr}_2$ ) (99%, Acros Organics), ethyl 2-bromoisobutyrate (EBiB, 98%, Acros Organics) and diethyl ether ( $\geq 99.0\%$ , Sigma Aldrich) were used without further purification.

For the AGET-ATRP polymerization of AN,  $\text{CuBr}_2$  (0.272 g) and HMTA (0.340 g) were added in a flask containing AN (2.0 ml, 30.4 mmol) to form the complex system. Then the initiator (EBiB) was added to the mixture. The resulting mixture was stirred under inert atmosphere using nitrogen purging; afterwards, the solution was slowly injected into to an aqueous solution of the surfactant Brij 35 (3.224 g, dissolved in 30 ml of distilled water) to form a transparent microemulsion. After purging the microemulsion with nitrogen for 30 min, the flask was immersed in an oil bath at  $80^\circ\text{C}$ . Then, 20 ml of deaerated aqueous solution of VC (0.321 g, 1.824 mmol) were added drop wise into the microemulsion in order to initiate polymerization. 20 min later, the rest amount of AN (6 ml, 91.2 mmol) was added to the ongoing latex system. The reaction was stopped after 2 h by immersing the flask into an ice bath. The polymer was precipitated in diethyl ether. The final product was purified by passing through alumina column to remove copper and dried under vacuum.

For the AGET-ATRP block copolymerization of AN with MMA, an *ab initio* emulsion ATRP was initiated using the procedure described above. The second monomer (MMA) (13 ml, 121.8 mmol) was added to the reaction after 2 hours. The reaction continued for 24 hours following the same aforementioned procedure. The purification of the copolymer was achieved by passing the product through alumina column in order to remove copper and dried under vacuum.

The structure of the polymers synthesized was studied using Fourier transform infrared (FTIR) spectroscopy (BioralExcalibus Series FTS 3000 MX). The polymer molecular weight distribution was determined via Gel Permeation chromatography (GPC) using dimethyl formamide ( $40^\circ\text{C}$ , flow rate=1.0 mL/min) as eluent. GPC consisted of a Waters 510 pump, four  $\mu$ Styragel cross-linked polystyrene columns (pore size  $10^2$  to  $10^6$  Å), and a Waters 410 differential refractometer detector.

### Results and Discussion

The PAN block copolymers synthesized via ATRP polymerization method has been proven that can be carbonized, and they have been investigated as precursors for porous carbonaceous materials with controlled porosity and improved electrochemical performance. The method has been termed soft (or organic-organic) templating. This can be achieved by using immiscible sacrificial blocks with PAN such as poly(*n*-butyl acrylate) (PBA): upon pyrolysis the PBA block chains are totally transformed to gaseous byproducts and the PAN chains are carbonized, leaving behind a porous material. The porosity of the residual depends on the morphology of the initial block copolymer [14]. This approximation seems quite promising also for synthesizing block copolymers that could be oxidatively stabilized faster and more efficiently than the currently random PAN copolymers used as precursors for the production of CFs.

In the current study, the technique “one-pot”, “two-step” was used in order to synthesize PAN block copolymers via AGET ATRP method. Matyjaszewski's group firstly carried out this technique of ATRP in a microemulsion system resulting in the preparation of stable translucent microlatexes [15]. Specifically, the AGET ATRP method is described as two-step *ab initio* microemulsion. The first step leads to the formation of a microemulsion polymerization template before the initiation of polymerization. In the micelles formed all ATRP components were encapsulated: catalyst, initiator and a small amount of monomer. After the activation of the catalyst and the initiation of the reaction, a second batch of monomer is added. During the reaction, the monomer diffuses from the monomer droplets to the polymerizing micelles containing the catalyst and the growing polymer chains. In this active emulsion system, the sequential addition of other monomers (after a certain length of time) leads to diblock or even multiblock copolymers, proving the reaction is actually living polymerization. The method applied resembles the typical *ab initio* emulsion polymerization; however, the serious problem due to the transportation of the Cu-based catalyst from the monomer droplets to the micelles/polymerizing particles through the aqueous continuum is ameliorated [16].

Figure 2 presents the FTIR spectra of PAN-b-PMMA copolymer. The most important peaks are at  $2950\text{ cm}^{-1}$  that is attributed to the  $-\text{CH}_2-$  and  $\text{CH}_3-$  units, at  $2240\text{ cm}^{-1}$  that is ascribed to the nitrile group,  $\text{C}\equiv\text{N}$ , at  $1740\text{ cm}^{-1}$  due to carbonyl groups,  $\text{C}=\text{O}$ , between  $1470$  and  $1370\text{ cm}^{-1}$  that is attributed to various C-H absorption modes, in the ranges of  $1240$ – $1060\text{ cm}^{-1}$  and  $920$ – $880\text{ cm}^{-1}$  that both ascribed to various absorption modes of C-O-C ester bonds [17]. Their presence indicate that the polymer contains both AN (i.e. nitrile-containing) and MMA (i.e. ester-containing) units.

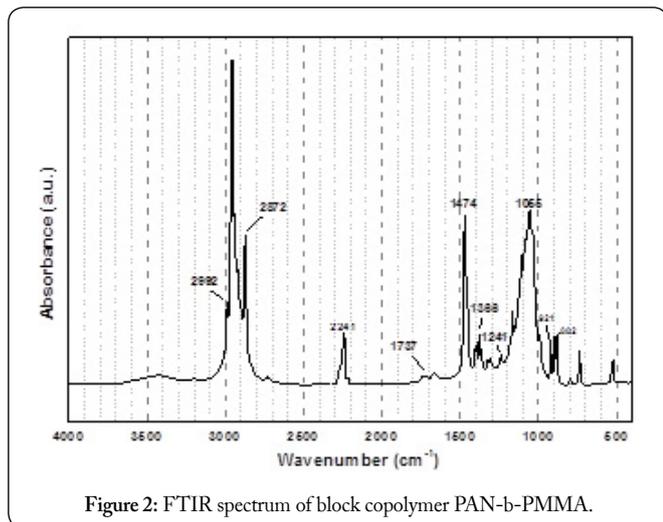


Figure 2: FTIR spectrum of block copolymer PAN-b-PMMA.

Figure 3 illustrates the GPC traces of (a) PAN homopolymer and (b) PAN-b-PMMA copolymer synthesized using AGET ATRP. Considering these GPC chromatographs it is clearly denoted that the peak attributed to the copolymer appears in shorter elution time compared to that of the homopolymer, indicating larger hydrodynamic volume due to the presence of two blocks joined together. Regarding the molecular weight distribution for the aforementioned homopolymer and copolymer, it may be remarked that the different shapes of the curves indicate that the PAN-b-PMMA copolymer has different molecular weight distribution than PAN homopolymer. This can be attributed to the grafting of PMMA blocks having different length onto PAN macromolecules with variable molecular weights: indeed, the curve of PAN-b-PMMA looks like a peak grown over a second peak. Thus, the combination of AGET-ATRP with the microemulsion technique is an effective method for synthesizing PAN copolymers with tailored structure.

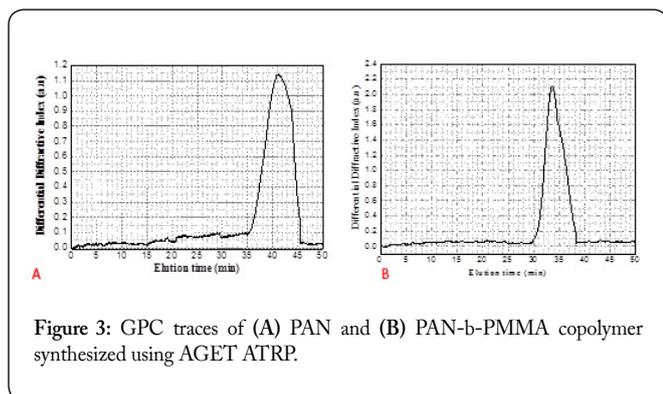


Figure 3: GPC traces of (A) PAN and (B) PAN-b-PMMA copolymer synthesized using AGET ATRP.

## Lignin and Lignin-Based Polymers as Precursors

### Experimental

Softwood Kraft Lignin (SKL) was obtained from Westvaco Corp. (Indulin AT, MWV); for comparison, a second commercialized SKL was also studied (Biochoice®, from Domtar). Hydrochloric acid (HCl 37%, Fisher Chemicals), poly(ethylene oxide) (PEO,  $M_n=100,000$  Da, Sigma Aldrich) and isotactic polypropylene (PP,  $M_n\sim 12,000$  Da, Sigma Aldrich) were used without any further purification.

Initially, lignin was acid modified by repeatedly washing with 2M HCl solution, followed by drying and grinding to fine powder. A blend of PEO/lignin with weight ratio 80/20 w/w was prepared by mechanical mixing in a Brabender compounder at  $110^\circ\text{C}$ . In order to blend with PP, lignin was alkylated by reacting with bromododecane in isopropanol. Before use, the alkylated lignin was washed with hydrochloric acid solution (in order to be neutralized), rinsed with water and dried under vacuum. Finally, the alkylated lignin was blended with PP in weight ratio PP/lignin: 80/20 w/w in a Brabender compounder at  $190^\circ\text{C}$ .

Thermal behavior of lignin (Indulin AT & Biochoice) was studied by thermo gravimetric analysis (TGA) which was performed under inert (nitrogen) and air atmosphere in a Mettler Toledo 815E thermobalance. The structure of the blends was investigated by FTIR measurements (BioralExcalibus Series FTS 3000 MX). Differential Scanning Calorimetry (DSC) measurements of the blends were performed with a TA Instruments Q200 under nitrogen atmosphere in the temperature range  $-90^\circ\text{C}$  to  $200^\circ\text{C}$  (scanning rate:  $10^\circ\text{C}/\text{min}$ ). Prior the measurement, the samples were heated to  $180^\circ\text{C}$  to erase their thermal history.

### Results and Discussion

Initially, the pyrolysis behavior of the two commercial SKLs (originating from different stock) was investigated by heating up to  $1000^\circ\text{C}$  in inert atmosphere (heating rate:  $10\text{ K}/\text{min}$ ). Figure 4 presents the weight loss and the weight loss rate (i.e. first derivative) of the two lignin samples. Generally, these materials had similar weight loss behavior; however, a more detailed analysis showed that there are some important differences between them. Firstly, Indulin AT produced somewhat higher pyrolysis residual (about 45%, compared to about 35% for BioChoice). It should be mentioned that similar values (i.e. between 35 and 45%) have been recently reported for a hardwood lignin and two other Kraft lignin [2, 4]. Part of the residue was due to the higher amount of inorganics in the former than the latter; however, the difference in pyrolysis residual between the two lignin samples is about 5%, which is three times the difference of inorganics amount (reported ash content: 2.4% for Indulin AT, 1.0% for BioChoice, [18]). Thus, it may be remarked that Indulin AT seems (at least initially) slightly better CFs precursor.

Regarding the initial weight loss of these materials (i.e. up to  $200^\circ\text{C}$ ), the humidity content was found to be around 2.0%. Moreover, the second peak of the weight loss rate at around  $150^\circ\text{C}$  could be attributed to the presence of crystallized water

inside lignin. The sharp weight loss at the range of 200°C up to 520°C is ascribed to the primary lignin pyrolysis. The temperature region is quite extended (i.e. about 300°C), the weight loss rate has a rather broad peak and the shape of the curve indicates that it is the result of 2 (or even 3) convoluted peaks. The aforementioned indicate that the decomposition is a multi-step process and the reaction kinetics is complex. During decomposition, lignin lost a large mass percentage as gaseous by-products. Even though the composition of the volatiles is unknown, given the large oxygen content of lignin, it can be assumed that the gaseous fraction is composed mainly of oxygen-containing molecules (mainly CO and CO<sub>2</sub>). By comparing the two feedstock materials, Indulin AT has somewhat smaller weight loss and has less sharp loss rate peak than BioChoice. This indicates that the pyrolysis proceeds more smoothly in the former than the latter, which is again an indicator that Indulin AT is a more suitable CF precursor. After the main decomposition, the weight loss rate decreased slowly. This step was due to progressive condensation of polyaromatic structures of the primary residual. This trend continued until about 800°C; at that point, an abrupt weight loss step appeared and the curve of weight loss rate presented another peak. This could be attributed to the onset of the secondary pyrolysis of the residual. During this step, the material lost the residual hydrogen in the form of hydrocarbon gasses (e.g. CH<sub>4</sub>, H<sub>2</sub>C=CH<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> etc.). Again Indulin AT fares better than BioChoice, losing about 3% (compared to 5% for the latter), even though the weight loss rate has a larger initial peak. This could possibly mean that the primary residual of Indulin AT contained a higher amount of hydrogen.

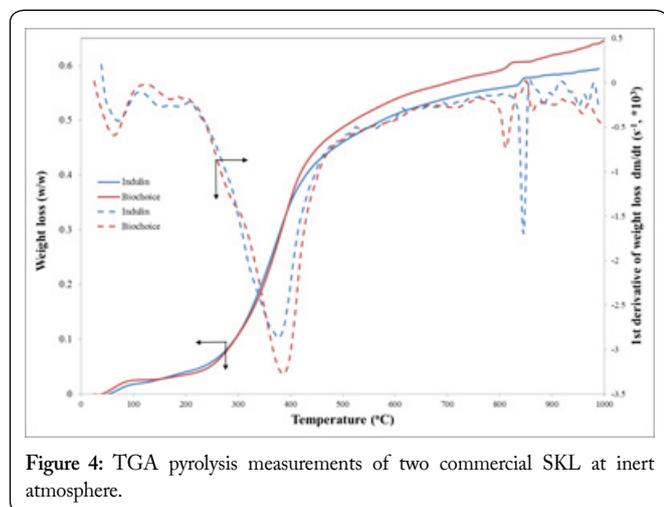


Figure 4: TGA pyrolysis measurements of two commercial SKL at inert atmosphere.

Even though the yield of 45% pyrolysis residual for lignin is acceptable, it is important to improve it even further and this can be achieved by oxidative stabilization. This is a similar process to the process of PAN-based CF production, while in case of lignin the proposed method consists of very prolonged heating (reported duration: up to 100 h) in the region 200–300°C using air atmosphere. It seems that the main barrier for this prolonged stabilization is the tendency of monofilaments to fuse with one another [2, 19]. A study of the conducted phenomena during this oxidative stabilization will assist the process amelioration. Figure 5 depicts the isothermal measurements of Indulin A Tat temperatures of 250 and

300°C in air atmosphere. The sample was heated with 50 K/min up to the final temperature and maintained there for 1 h (3600 s). The weight loss curves demonstrate that there was an abrupt initial weight loss during the fast heating, followed by a slow weight loss with decreasing rate (i.e. first derivative tended towards zero from negative values). As expected, the initial weight loss and the weight loss rate were higher at 300°C than 250°C. By comparing the abrupt initial weight loss at 250 and 300°C with the weight loss at the same temperatures during scanning up to 1000°C, the former were clearly higher than the latter, i.e. the weight loss was 10.4% compared to 5.3% (at 250°C) and 16.6% compared to 10.8% (at 300°C).

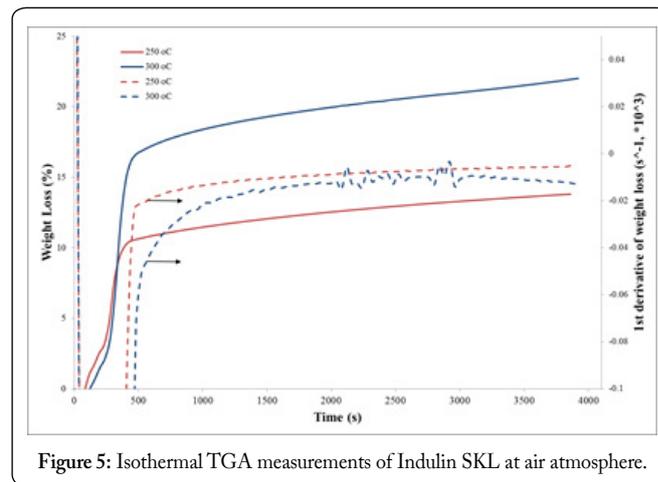


Figure 5: Isothermal TGA measurements of Indulin SKL at air atmosphere.

These differences could be attributed to the oxygen of air atmosphere, which incurred considerable oxidation reactions. However, it should be noted that the following isothermal measurements indicate that lignin was essentially stabilized afterwards, losing only an extra 3.4% (at 250°C) and 4.4% (at 300°C) of its mass during the heating for an additional hour. Even if the heating continued for more time, it is expected that the material would not loose considerably more than that amount, since the weight loss rate tends towards null. Practically, the material had lost all its volatile content (i.e. the amount that could be evolved at that particular temperature) and the structure became increasingly more heat resistant (for that particular temperature).

Acid treatment of lignin contributes to the reduction of hydroxyl groups with simultaneous increase of C=O functions. Specifically, the acid-treated lignin that arises from the cross-linking of native lignin shows an increase of the phenol to aliphatic hydroxyl ratio and a reduction of total hydroxyl content of lignin [20, 21]. The effect of acid treatment on the structure of lignin was investigated using FTIR, as presented in Figure 6. The broad band at 3000–3700 cm<sup>-1</sup> is attributed to hydroxyl group of phenolic and aliphatic structures. The bands centred on 3000–2840 cm<sup>-1</sup> arise from various C–H bonds in the aromatic methoxy groups and in the methyl and the methylene side groups. The characteristic absorption bands for aromatic rings of lignin are at 1596 cm<sup>-1</sup>, 1518 cm<sup>-1</sup> and 1410 cm<sup>-1</sup>. The first peak also signifies the presence of a conjugated structure [4, 21]. Even though the two spectra are generally similar, they have several differences between them.

Firstly, a peak centred at around 1690 cm<sup>-1</sup> appears after

treatment, but this seems to be attributable mainly to the decrease of the peak at  $1596\text{ cm}^{-1}$  after the treatment, than to growing of a novel peak. These differences indicate that the acid treatment (apart from the reduction of hydroxyl groups) caused as a side effect the decrease of conjugated structures in lignin. It also looks like that in acid treated lignin there is a shoulder at  $1711\text{ cm}^{-1}$ , corresponding to carbonyl groups.

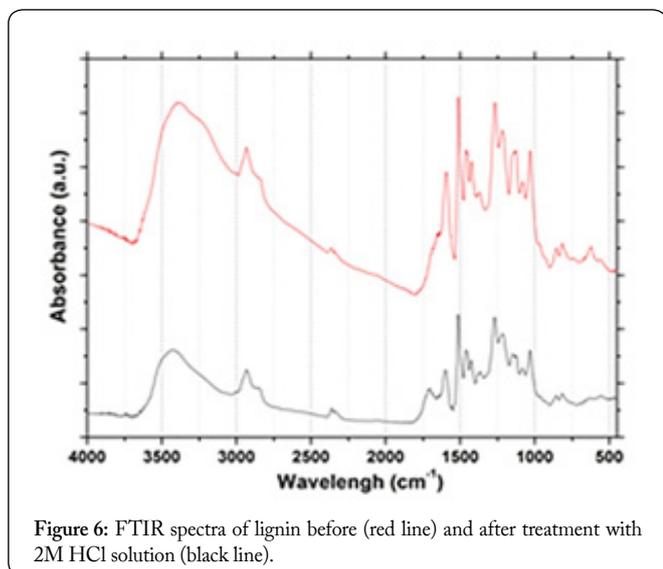


Figure 6: FTIR spectra of lignin before (red line) and after treatment with 2M HCl solution (black line).

The blends of the lignin with PEO and PP were macroscopically homogeneous (i.e. they were one phase). Figure 7 depicts the FTIR spectra of blends. A broad band at  $3261\text{--}3589\text{ cm}^{-1}$  is attributed to the hydroxyl groups of lignin. Between  $2990$  and  $2840\text{ cm}^{-1}$  the peaks are attributed to methyl and methylene groups of PP backbone chain. Moreover, the absorptions peaks of aromatic methoxy, methyl and methylene groups of side chain of lignin appear in the same region. The absorption bands of lignin are found at  $1690\text{ cm}^{-1}$ ,  $1518\text{ cm}^{-1}$  and  $1410\text{ cm}^{-1}$  (aromatic vibrations). The peak at  $1471\text{ cm}^{-1}$  arises from C-H deformation vibration in  $-\text{CH}_3$  and  $-\text{CH}_2$  for both lignin and PP. The peak at  $1170\text{ cm}^{-1}$  is related to C-H in methyl, methylene and methane groups of PP. In the case of lignin/PEO blend the spectrum is similar [22]. Thus, it is clear that in both blends the spectra are dominated by the respective thermoplastic (i.e. PEO or PP); this is not surprising, given that they were the majority component.

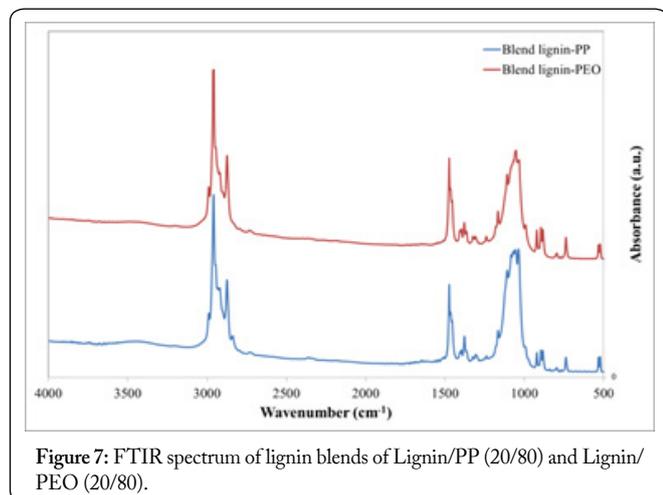


Figure 7: FTIR spectrum of lignin blends of Lignin/PP (20/80) and Lignin/PEO (20/80).

The thermal properties of the lignin blends with thermoplastics were investigated using DSC. Figure 8 illustrates the DSC curves of the lignin/PEO blend recording a sharp exothermic peak during heating and a sharp endothermic peak during cooling. These phenomena are attributable to melting and crystallization of PEO, respectively (reported in the range  $57\text{--}73^\circ\text{C}$ ).

Lignin can be extracted from several materials, having different properties depending on its origin. The glass transition temperature ( $T_g$ ) is reported to appear as low as  $91^\circ\text{C}$ – $97^\circ\text{C}$  for Organosolv lignin or up to  $174^\circ\text{C}$  for Kraft lignin. Penkina et al. [22] studied Indulin AT and reported that the  $T_g$  varies from  $135^\circ\text{C}$  to  $142^\circ\text{C}$ . The presence of sharp peaks for both heating and cooling indicates good mixing of lignin with PEO. Despite the fact that  $T_g$  of modified lignin is reported at  $143^\circ\text{C}$ , no glass transition was observed during the DSC of the blend, probably due to the high dilution of lignin. Similarly to L/PEO, lignin/PP (L/PP) blend exhibited melting and crystallization peaks, as well as a glass transition attributable to PP. The difference was that melting was a double peak (i.e. at  $149^\circ\text{C}$  and  $157^\circ\text{C}$ ). This phenomenon could be ascribed to possible segregation of PP crystallites during blending, caused by the presence of lignin (which is still solid at that temperature), leading to the formation of crystallites of different size.

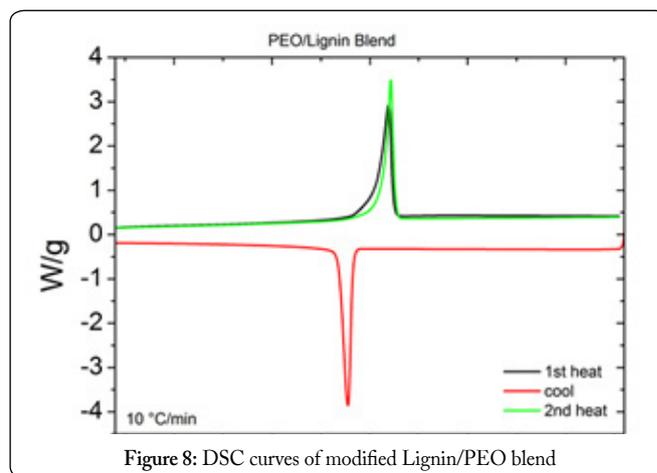


Figure 8: DSC curves of modified Lignin/PEO blend

Table 2: Transition temperatures of Lignin/PEO and Lignin/PP blends.

Material	$T_g$ ( $^\circ\text{C}$ )	$T_m$ ( $^\circ\text{C}$ )	$T_c$ ( $^\circ\text{C}$ )
Lignin	143	-	-
Lignin/PEO (20/80)	N.O.	60	39
Lignin/PP(20/80)	45	149 / 157	117

$T_g$  = glass transition temperature,  $T_m$  = melting temperature,  $T_c$  = crystallization temperature, N.O. = not observed.

These initial results on the pyrolysis of lignin clearly denote that lignin has a high pyrolysis yield and could be effectively introduced as CFs precursor. Additionally, the results of weight loss during oxidative isothermal treatment demonstrate that the effective stabilization does not demand prolonged heating. Despite the fact that blending lignin with thermoplastics such as PP and PEO revealed that it is important to further study the procedure, the latter could be used as a proper spinning method for lignin.

## Conclusions

In order to improve different aspects of the CFs production, two different approaches were applied: (1) developing novel tailored PAN block copolymers (as a means for improving the quality of CFs) and (2) study the introduction of lignin (a renewable and sustainable material) as a viable CFs precursor. The initial research results for these two approximations demonstrated, respectively, that: (1) it is possible to synthesize acrylonitrile based copolymers with specified structure using the AGET-ATRP polymerization method in microemulsion system, (2) lignin produces high carbonaceous residual upon pyrolysis, it is not necessary to have prolonged oxidative stabilization and it is feasible to blend lignin with thermo plastics such as PEO that could be spun into lignin fibers. Thus far, both these methodologies exhibited potential and will be further developed towards industrial application.

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