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Effect of boric acid on the stabilisation of cellulose-lignin filaments as precursors for carbon fibres.

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Abstract: The increasing demand for a low-cost and renewable carbon fibre precursor has driven the focus on bio-based precursors. Cellulose-lignin composite fibres are a new approach toward this direction. The combination of cellulose and lignin into a composite fibre could solve some of the current limitations for pure cellulose and lignin fibres. This study investigated the treatment of the composite fibres with boric acid with focus on carbon yield, stabilisation rate and fibre fusion, which is a typical defect in carbon fibre production. The influence of boric acid on the mechanism of stabilisation was studied. The stabilisation time was reduced by 25% through treatment with the reduction of fibre fusion, while the carbon yield increased significantly in comparison to the untreated fibres.

Keywords: Biopolymer, low-cost carbon fibres, cellulose-lignin composite fibres, boric acid, fibre fusion.

1. INTRODUCTION:

The boom in the electric mobility and wind energy industries has greatly increased the demand for carbon fibre primarily because of its inherent lightweight and high strength properties. Its high cost, however, continues to inhibit wider usage driving research into the development of new low-cost carbon fibre (Downing 2013; Frank et al. 2014; Choi et al. 2019). The production of carbon fibre is a multi-step process starting with the initial spinning of a precursor or “white” fibre, its oxidation or stabilisation, through to carbonisation to produce carbon or “black” fibre. The precursor accounts for about 50% of the production cost, which has focused a lot of research on the use of alternative precursors to polyacrylonitrile (PAN), the most common precursor of all and industry standard, to further reduce cost (Morgan 2005; Frank et al. 2014). Some proposed alternative precursors include polyethylene (Choi et al.

2019), cellulose (Byrne et al. 2016) and lignin (Baker 2010; Ogale et al. 2016), with the latter two gaining the most attention because of their potential low cost and sustainability, being obtained from renewable resources. Unfortunately, cellulose and lignin individually have several disadvantages that to date has prevented them from fulfilling much of their potential. Cellulose-based carbon fibres, despite being the first synthetic man made carbon fibre (Morgan 2005; Frank et al. 2014), has a low carbon yield while lignin based carbon fibres require a very long stabilisation time (Morgan 2005; Frank et al. 2014; Ogale et al. 2016). The combination of cellulose and lignin into a composite or blended fibre, however, has shown that some of these disadvantages can be overcome, paving the way for the development of a new low-cost sustainable carbon fibre. Recent examples have shown that when blended together the composite fibre can indeed produce a high carbon yield and be stabilised in a much shorter time (Ma et al. 2015; Byrne et al. 2016; Olsson et al. 2017). Furthermore, it has been shown that when using a continuous dry-jet spinning method, the filaments display a high level of molecular orientation imparting excellent mechanical properties to the composite fibre (Ma et al. 2015) which is highly desirable for the subsequent carbon fibre manufacture (Morgan 2005; Frank et al. 2014). This promising new spinning method provides sufficient flexibility to introduce a variety of different cellulose and lignin fibre compositions.

Stabilisation is a process that converts precursors into thermally stable filaments that can withstand high-temperature carbonisation (Morgan 2005; Frank et al. 2014). The stabilisation process for cellulose and lignin is normally conducted in an oxidative environment, mostly in air but sometimes in oxygen. An oxidative environment speeds up thermal pyrolysis of cellulose compared with an inert atmosphere such as nitrogen (Strong 1974), while for lignin the oxidation process is necessary to increase cross-linking which is crucial to inhibiting or preventing the melting and subsequent fusion of the fibres during high temperature carbonisation. Melting and fusion have an extremely deleterious impact upon the final properties of the lignin-based carbon fibre (Frank et al. 2014; Ogale et al. 2016). Despite the advantages of composite lignin and cellulose fibres, their stabilisation remains comparatively slow and the challenge to prevent fibre fusion remains. To address these issues, flame retardants have been used as catalysts to speed up the stabilisation process and increase the carbon yield for cellulose-based carbon fibres (Schuyten et al. 1955; Lewin 1985). In much the same way as flame retardants which operate in the condensed phase to increase char yield of a polymer and reduce combustion, common flame retardants based upon boron compounds (boric acid and borax) and phosphorus compounds have been shown to enhance stabilisation of lignin and cellulose by increasing the rate of decomposition and crosslinking, which ultimately aids carbonisation. Typically performed by applying these flame retardants to a precursor by passing the tow through a solution in water before drying (Morgan 2005), Karacan et al. showed that rayon fibres treated with a mixture of phosphorus and boric acid significantly improved oxidative stability while reducing the evolution of volatile compounds. However, no specific details in regards to the stabilisation mechanism, carbon yield or stabilisation rate was discussed (Karacan and Soy 2013). Byrne et al. treated regenerated cellulose samples with a phosphorus-based ionic liquid showing a significant improvement in the carbon yield (50% remaining after carbonisation at 500°C). The alternation in the degradation pathway from thermal depolymerization to arrangement and crosslinking leads to this significant improvement (Byrne et al. 2014). However, using ionic liquids is a more expensive approach than water-based solutions. For cellulose-lignin composite fibres, Bengtsson et al. 2019 treated them with a phosphorus-based flame retardant (ammonium dihydrogen phosphate) (Bengtsson et al. 2019) revealing a significant increase in carbon yield despite a reduction in mechanical properties of the final carbon fibre. Finally, Zhang et al. 2016 succeeded in increase the tensile strength of wood-based carbon fibres by 45% by impregnation with boric acid (Zhang et al. 2016). The treatment had changed the carbon structure by increasing the graphitization level as well as reducing the defects in carbon structure, but again the stabilisation mechanism for wood-based carbon fibres were not discussed. Clearly, the influence of the catalyst on the stabilisation process in preparation for carbonisation is an important area of research as a promising alternative strategy to reduce stabilisation times, increase carbon yield and improve the properties of the final carbon fibre.

In this paper, cellulose-lignin composite fibres with 70 % cellulose and 30 % lignin were treated with boric acid before stabilisation. The impact of treatment on stabilisation parameters such as carbon yield, fibre fusion and rate were investigated. Furthermore, the decomposition mechanism promoted by boric acid treatment of the composite fibres in terms of reaction rate, volatile evolution and microstructure is discussed.

2. EXPERIMENTAL:

2.1 Preparation of treated fibres:

Precursor fibres were provided by Aalto University, Finland consisting of 70% pre-hydrolysed kraft birch pulp (Stora Enso Enocell mill in Finland) and 30% organosolv beech lignin (Lignocellulosic Biorefinery Pilot Plant, Fraunhofer CBP in Leuna, Germany) by weight. Both wood pulp and lignin were dissolved in 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH]OAc). The obtained dope was dry-jet wet-spun through an air gap of 1 cm before coagulation in a cool water bath (9±2°C). The treated fibres were prepared by soaking precursors in boric acid aqueous solution with different concentration (1%, 3% and 6% wt) at 80 °C for 5 min. After that, the fibres were wiped to remove the excess solution and dried at 80 °C in an air circulating oven until the weight was unchanged. The final increase in the weight of the fibre was less than 1% regardless of the boric acid solution.

2.2 Preparation of stabilised fibres:

Untreated and treated fibres were hung on a steel rack with an applied tension of 13.1 N/m. The tension was used to mimic the applied tension during the continuous production of carbon fibres. Samples were stabilised in air using a Binder FD53 oven set at 280 °C. Once the temperature had stabilised at 280 °C, samples were removed after 15, 30, 45 and 60 min.

2.3 Fourier-transform infrared spectroscopy (FTIR):

FTIR analysis was performed using attenuated total reflection (ATR) on a Bruker Lumos FTIR. Each spectrum was measured from 600 to 4000 cm^{-1} wavenumbers at a resolution of 4 cm^{-1} and consisted of 32 scans. Each sample was scanned 3 times in different locations on the fibre to determine the level of consistency.

2.4 Simultaneous thermal analysis - Fourier-transform infrared spectroscopy (STA-FTIR):

The gas emission during the thermal pyrolysis of fibres was analysed using a hyphenated system that couples a simultaneous thermal analysis instrument (STA 8000, Perkin Elmer) with a Fourier-transform infrared spectroscopy instrument (Frontier, Perkin Elmer). Around 5 mg of sample was pyrolyzed in a thermogravimetric analyser (TGA) in a N_2 atmosphere with a heating rate 20 °C/min from room temperature to 600 °C. The same sample amount was used for each measurement for semi-qualitative comparison of the evolved gas. FTIR analysis was then performed on the pyrolyzed gas over the range 500 to 4000 cm^{-1}, at a resolution of 2 cm^{-1}.

2.5 Scanning electron microscope (SEM):

The SEM measurements were conducted on a Zeiss Supra 55VP. For cross-sectional images, samples were mounted into a heat shrink tube before immersion in liquid nitrogen until frozen, then snapped using a sharp blade. The fibre diameter was measured from the cross-section of 10 filaments. For bundled images, a small section (4-5 mm) of the tow was cut and put on top of carbon tape. Samples were coated with gold before observation.

2.6 Thermal gravimetric analysis (TGA):

The TGA measurements were conducted on a TA Instruments Q50 Thermal Analysis. Each measurement used 4-5 mg of the sample and heated from room temperature to 500 °C at a heating rate of 20 °C /min in N_2 or air. For every samples, the TGA was conducted 3 times and the carbon yield was calculated by subtracting the weight loss peak before 100°C that accounts for absorption water.

3. RESULTS AND DISCUSSION:

3.1 Chemical changes of precursors after treatment with boric acid:

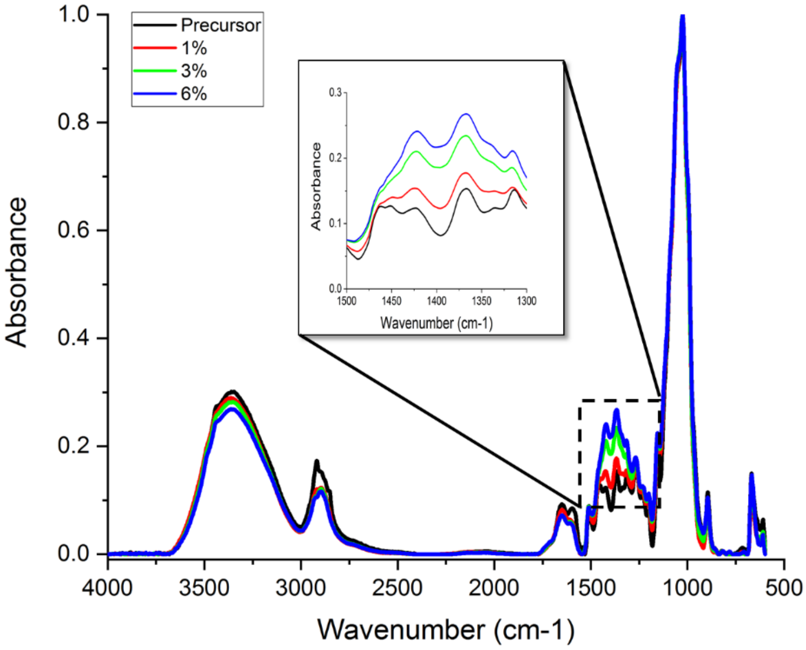

Figure 1: FTIR spectra of 30% lignin-70% cellulose fibres indicating the chemical changes when treated with boric acid at different concentrations. Spectra are normalized at the C-O-C peak at 1200 cm^{-1}.

The precursor fibres were immersed in the boric acid solution at different concentrations (1%, 3% and 6%) for 5 min at 80 °C. The FTIR results of treated fibres after drying are shown in Figure 1. Although peaks in the spectra from boric acid are difficult to observe due to overlapping B-O and B-O-H bands with C-O and C-O-H bands (Peak et al. 2003; Shawgi et al. 2017), their increasing intensity at 1420 cm^{-1} and 1365 cm^{-1} (B–O stretching) (Romanos et al. 2013; Shawgi et al. 2017) indicates that boric acid was successfully incorporated into the precursor fibre. Both cellulose and lignin contain hydroxyl groups, so it is reasonable to expect the fibre surface will have extensive hydroxyl groups originating from the D-glucose groups of cellulose (Morgan 2005; Frank et al. 2014) and phenolic groups from lignin (Frank et al. 2014; Ogale et al. 2016). The two likely processes occurring between boric acid and the O-H groups of the fibre surface are boric acid esterification from either cellulose or lignin (Figure 2a) and non-covalent bonding via hydrogen bonding (Figure 2b). Boric acid is known to react with polyol compounds to form a tetrahedral ester including a cis vicinal diol structure (Weser 2008; Pappin et al. 2012), which forms a stable chelate with boron. However, this structure does not exist in the D-glucose unit of cellulose or lignin, so it is more likely that boric acid reacts with cellulose and lignin as described in Figure 2a. It is proposed that both processes will readily occur on the fibre surface potentially limiting the penetration of boric acid into the composite fibres.

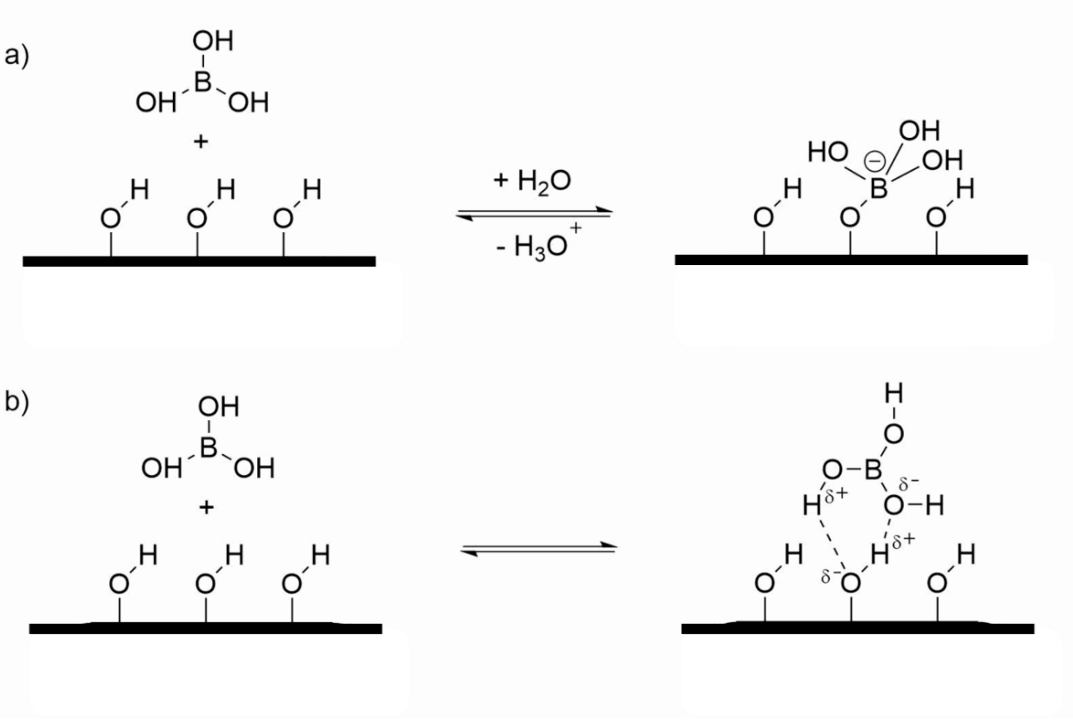

Figure 2: Interaction between boric acid and precursor a) esterification reaction b) hydrogen bonds

3.2 Influence of boric acid treatment on the carbon yield:

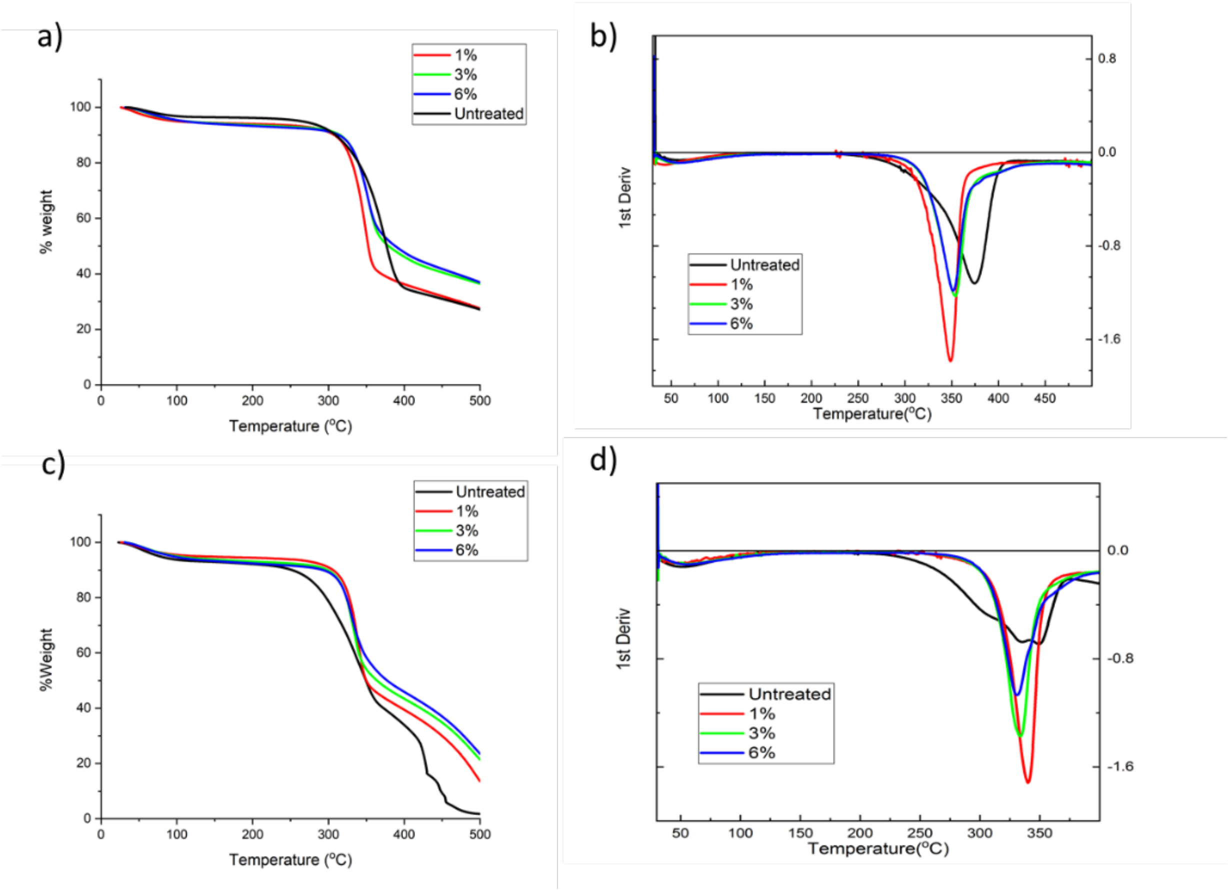

Figure 3: a) TGA in nitrogen and b) its 1^st^ derivative c) TGA in air and d) its 1^st^ derivative of the composite fibre consisting of 30% lignin and 70% cellulose.

As mentioned above, boric acid treatment has previously been used in cellulose-based carbon fibres to increase the carbon yield of the pyrolysis (Morgan 2005; Frank et al. 2014; Choi et al. 2019). In this study, TGA was used to quantify its influence on the carbon yield during pyrolysis in different atmospheres, both oxidative (air) and non-oxidative (nitrogen). In nitrogen, the samples treated with 3% and 6% boric acid show a similar increase in carbon yield up to around 37% from 27% of the untreated sample, while the sample treated with 1% appears not to improve the carbon yield at all when compared to the untreated sample (Figure 3a). However, the first derivative curve (DTG), a reflection of the rate of degradation, indicates that even when applying the 1% boric acid solution, the rate of pyrolysis is faster than the untreated sample (Figure 3b). The derivative peak for the pyrolysis reaction for the treated sample is at 300 °C while the peak for the untreated sample is 50 °C higher at 350 °C. This provides further evidence that boric acid is indeed acting as a catalyst to speed up thermal pyrolysis of the precursor even at the lowest concentration of acid treatment (1% boric acid) (Morrey 2003; Roth et al. 2007).

In air, the pyrolysis reaction for all samples starts earlier and is finished significantly faster than compared with nitrogen as a consequence of the oxidative environment (Figure 3d) (Strong 1974; Byrne et al. 2018). Unexpectedly, the untreated sample degrades before the treated samples by about 30 °C with little effect upon the concentration of boric acid (around 290°C and 320 °C, respectively). A possible reason for this is that boric acid forms a protective layer on the fibre surface inhibiting oxygen diffusion (LeVan and Tran 1990; Morrey 2003), and increasing ignition temperature (Kozłowski and Muzyczek 2020) complementing the above mentioned hypotheses of chemical reactions. Despite this, the DTG curves show that the treated samples still pyrolyze at a faster rate than the untreated sample once degradation is initiated. Another point to note for the oxidative pyrolysis is that when the temperature increases beyond 400 °C, the untreated sample degrades completely leaving no char at all, yet the treated samples display a significantly higher amount of char, between 15% and 30% at 500 °C (Table 1). This clearly emphasizes the role of boric acid in promoting char formation through catalysing dehydration reactions (LEVAN 1984; Kandola et al. 1996) which promotes crosslinking and ultimately the quality of the fibre after carbonisation (LeVan and Tran 1990; Jagtoyen and Derbyshire 1998; Di Blasi et al. 2007). This is similar to how a flame-retardant based upon boron or phosphorous functions to reduce the flammability of a polymer. Increasing crosslinking in the char through dehydration and condensation reactions, produce a dense barrier preventing volatiles from migrating from the condensed phase into the gaseous phase and, hence reducing combustion.

In terms of carbon yield, the untreated sample burnt completely so there is no char at all. The sample treated with 1% boric acid solution had the lowest measurable char at 14.3%. The carbon yield for the sample treated with 6% boric acid solution had the highest, but for the sample treated with 3% boric acid solution it is similar to 6% at 23% (Table 1). This is likely explained by the surface of the fibres being effectively shielded from further penetration of boric acid as suggested above. It is also important to note that the FTIR spectra for the 3% and 6% boric acid solution are virtually identical. The increased carbon yield after boric acid treatment is highly desirable as this plays a critical role in reducing the overall cost of carbon fibre (Frank et al. 2014; Choi et al. 2019).

Table 1: Carbon yield at 500 °C as a function of boric acid concentration

	Untreated	**1%**	**3%**	**6%**
In nitrogen	30.81	32.28	41.12	42.14
In air	0	19.40	27.91	29.32

3.3 Influence of boric acid treatment on the gas emission of thermal pyrolysis

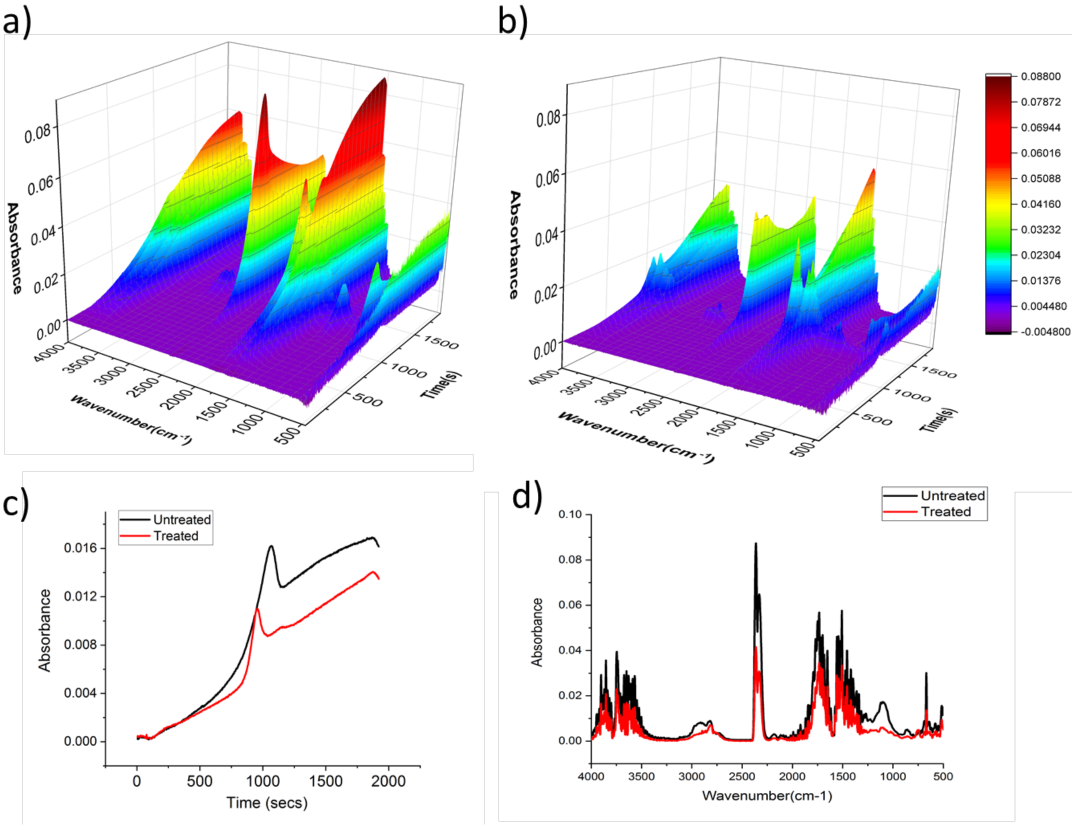

Figure 4: FTIR analyses of gas emission as a function of time for a) untreated b) treated samples; c) average intensity over time d) FTIR at peak of emission.

To further understand the influence of boric acid on the pyrolysis reaction of the precursors, the treated sample (3% boric acid) was compared to the untreated sample using a STA-FTIR hyphenated system. The gas evolving from STA was analysed by FTIR as a function of time. As shown in Figure 4a and b, the total amount of gas emitted from the treated sample is less than the untreated sample. Consequently, the carbon yield of the treated sample is higher than the untreated sample complementing the TGA results above. The peak of volatile emission shown in Figure 4c indicates that the untreated sample pyrolyzed more slowly than the treated sample. Figure 4d shows the FTIR spectrum taken at the peak of emission in Figure 4c. The emission band for O-H, which is mainly from H_2O (around 3748 cm^{-1}), and FTIR peaks for CO_2 (2369 cm^{-1}), C-H alkane (2922 cm^{-1}), C-O-C (1122 cm^{-1}) (Li et al. 2001; Yang et al.

2007) decrease after treatment with boric acid. Further investigation was made by plotting the absorbance of those peaks as a function of time (Figure 5).

Figure 5a shows the release of H_2O during the pyrolysis. Since the dehydration reaction was catalysed by boric acid, the treated sample released H_2O before the untreated samples did. Moreover, the peak for the untreated sample is broad while the treated sample peak is quite sharp. This indicates that the dehydration process occurs more rapidly for the treated sample, while for the untreated sample, it is a slower releasing process.

Figure 5b shows the release of CO_2 as a function of time. Similar to the untreated sample, the release of CO_2 clearly occurs via two separate processes, accounting for the two stages of pyrolysis. For the untreated sample, there is a peak followed by a longer tail, while for the treated sample these two processes appear more clearly as distinct peaks. The first peak occurs at the same time as the release of H_2O, suggesting it is related to dehydration of the precursor. Dehydration with the boric acid catalyst is shown to occur faster, so the first peak due to CO_2 evolution also occurs earlier, while the second peak related to thermal degradation of cellulose and lignin is unaffected, increasing their separation.

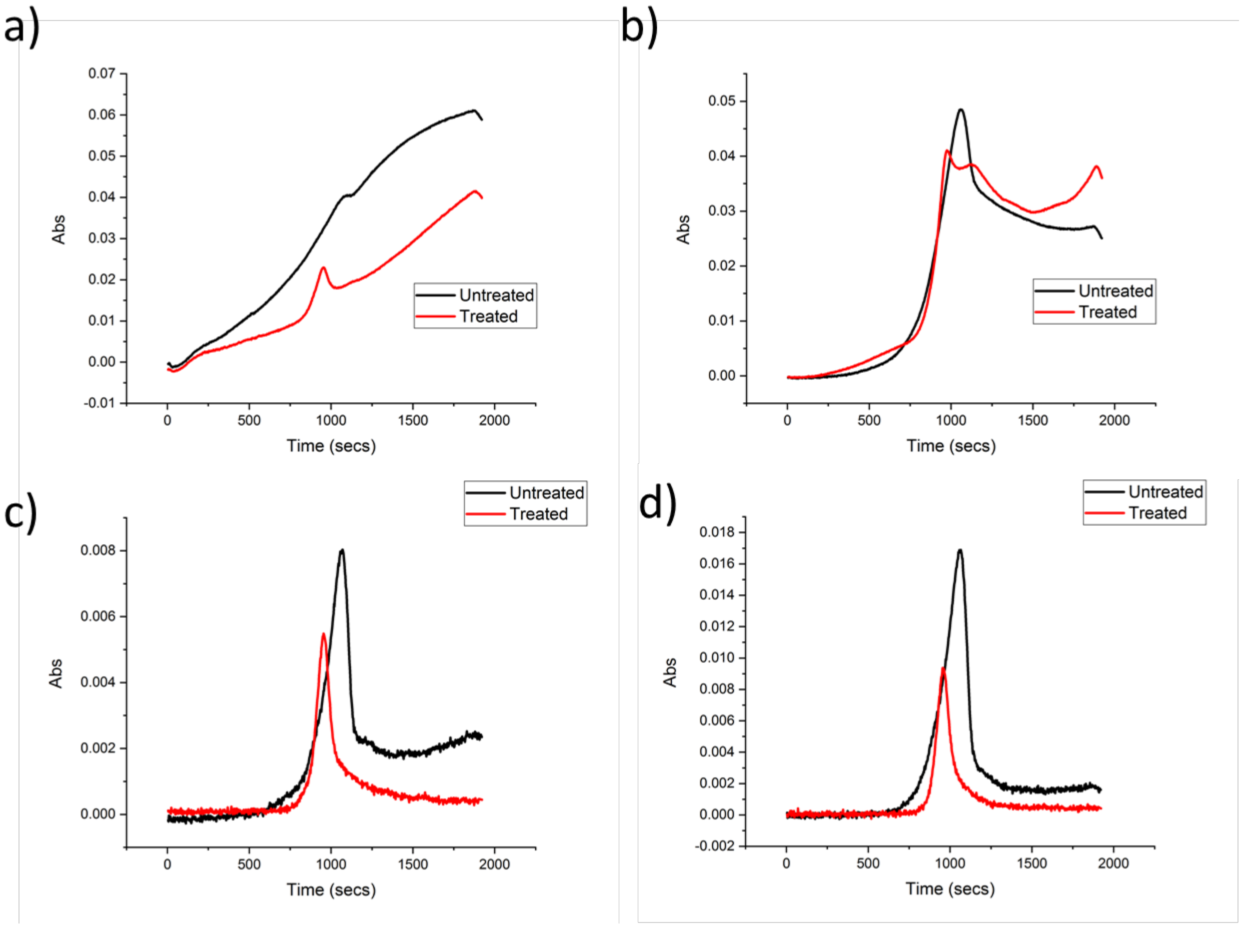

Figure 5: Absorbance as a function of time for a) H_2O (O-H peak) b) CO_2 c) CH d) C-O-C

Figure 5 c and d show the change in IR absorbance of C-H peak and C-O-C peak as a function of time. Both peaks account for complex compounds such as phenols, which are base units in lignin, and levoglucosan, which is a prominent pyrolysis product from cellulose(Bacon and Tang 1964). The release of such complex compounds is the main cause of low carbon yield, but as has been shown, the boric acid treatment increases char suggesting the formation of levoglucosan from cellulose is inhibited (Bridgwater et al. 1999; Di Blasi et al. 2007). Meanwhile, boric acid also causes change on how lignin decomposes, resulting in lower emission of phenols (Jagtoyen and Derbyshire 1998; Roth et al. 2007). Consequently, the implication is that boric acid reduces the release of phenols and levoglucosan, leading to increase in the carbon yield of the treated sample. Moreover, phenols and levoglucosan are flammable gases which can catch fire at high temperature, so a decrease in concentration will necessarily have a beneficial impact upon reducing the flammability of the composite fibres increasing the safety of the manufacture of carbon fibre from this method.

3.4 Influence of boric acid treatment on stabilised fibre morphology

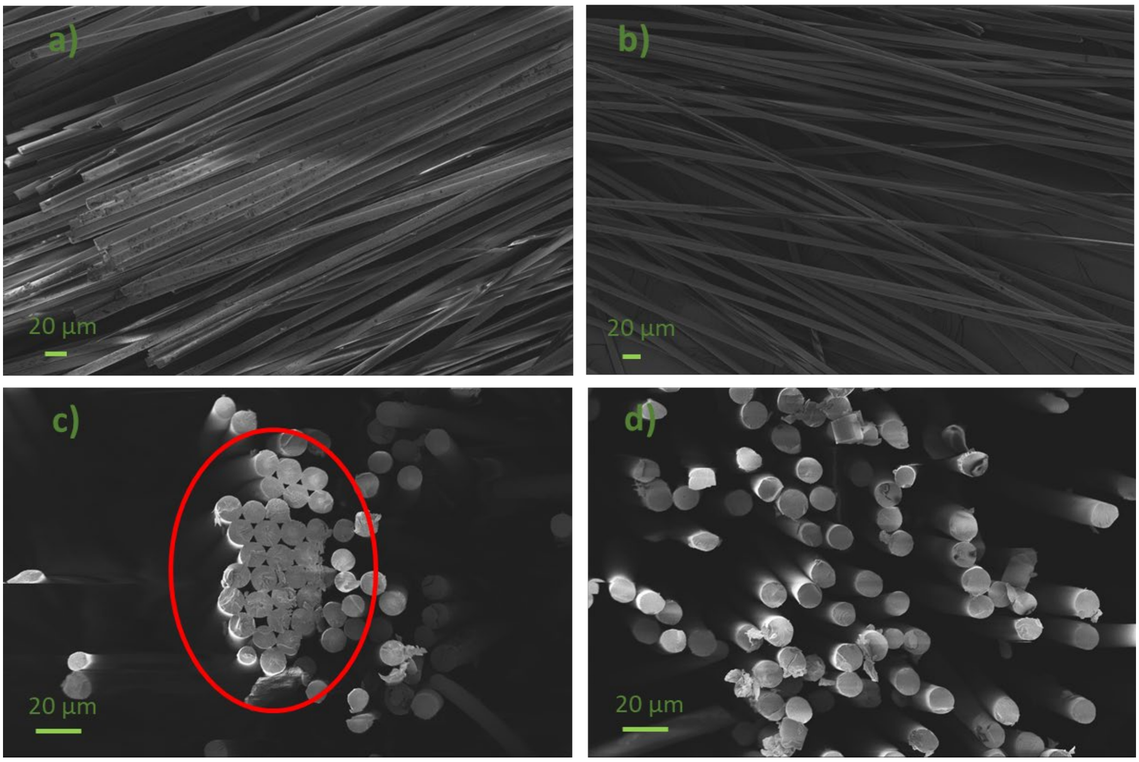

Figure 6: SEM images for fibre bundles of a) untreated and b) treated stabilised sample (250x magnification); cross-section of c) untreated and d) treated stabilised sample (700x magnification).

The gas emission during stabilisation not only relates to the carbon yield of the process but also influences its processability. Under tension during processing on a carbon fibre line, the gas evolved becomes trapped between the fibre tows, and degrades to form a tar resulting in an adhesive like substance between the filaments fusing them together (Ford and Mitchell 1963), which is obviously highly undesirable. Consequently, the fibres lose their flexibility and become fragile. As mentioned above, the treatment with boric acid reduces the amount of gas emitted, hence reducing this problem significantly. In this work, both treated and untreated samples were stabilised at 280 °C for 1 h under tension (13.1 N/m). The SEM images for both treated and untreated samples are shown in Figure 6. The untreated sample shows significant deposition of tar, evidenced by black marks on the surface of fibres (Figure 6a) compared to the more pristine and defect free appearance of the treated sample (Figure 6b). It is proposed that this deposition causes the heavy fusion of filaments of the untreated sample (Figure 6c). In contrast, fusion is effectively absent in the treated sample. Another profound effect of reducing gas emission is the increase of stabilised fibre diameter (Figure 7), which directly reflects the increase in carbon yield of the stabilisation process.

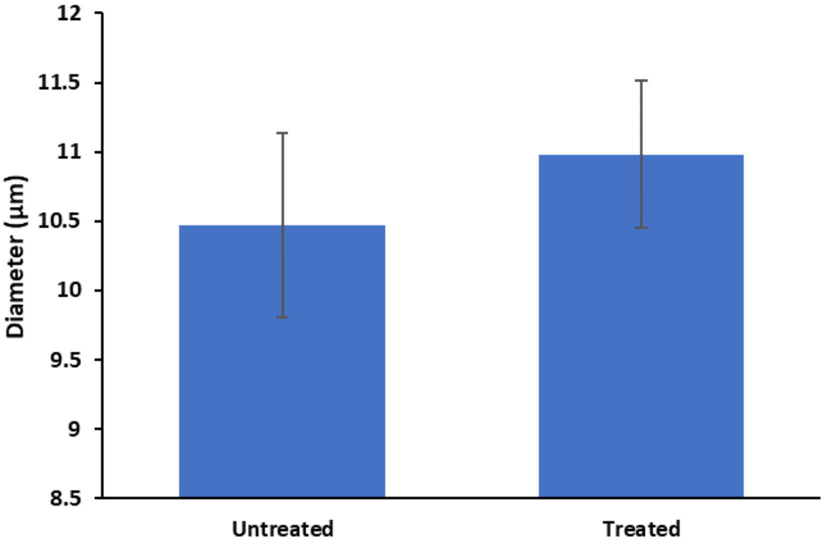

Figure 7: Fibre diameter for treated and untreated samples.

3.5 Influence of boric acid treatment on stabilisation rate:

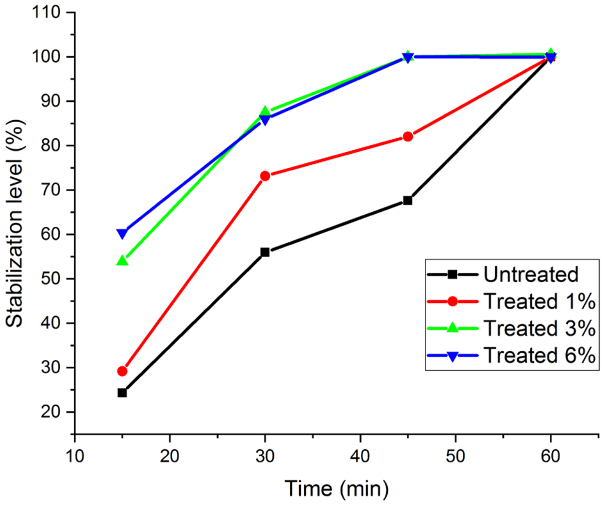

Figure 8: The relative stabilisation level at 280 °C as a function of time.

To measure the impact of boric acid treatment on the stabilisation rate, precursors were treated with different boric acid concentration (1%, 3% and 6%) and stabilised at different times (15 min, 30 min, 45 min and 60 min). The relative stabilisation rate was calculated based on the level of oxidation, which is determined from FTIR. The intensity of the C=O peak, which is an indicator for the oxidation, was normalized against the C-H peak, which is relatively stable during the stabilisation (Byrne et al. 2016). The calculated results are shown in Figure 8. The untreated sample has the slowest stabilisation rate. With a low concentration of boric acid treatment (1%), the stabilisation rate increases. The stabilisation rate further increases with 3% of boric acid, but with a higher concentration (6%), it remains unchanged. Finally, the effectively similar boric acid concentration of 3% and 6% may appear to have led to a similar stabilisation rate and is another benefit for carbon fibre production beside the increase in carbon yield given the potential to reduce production time and costs.

4. CONCLUSION:

In conclusion, composite cellulose-lignin fibres have been successfully treated with boric acid at varying concentration. The concentration of boric acid in the composite fibres increased when the treatment concentration increased. However, it reaches a plateau when the treatment concentration increased from 3% to 6%. The treatment with boric acid has increased the carbon yield from 27.4% to 37.4% for TGA measurements done under nitrogen atmosphere. It is a consequence of the increase in dehydration rate due to boric acid. For TGA measurements in air, the treatment shows a significant improvement in thermal stability for the composite fibres. The increase in thermal stability, which likely comes from a change in carbon structure, is a profound benefit when stabilised fibres are carbonised. Another profound effect of boric acid treatment is the reduction of emission gas, which increases not only carbon yield but also reduces the level of flammable gas. The reduction of flammable gas promotes the safety of carbon fibre production while it also decreases the environmental impact. Finally, the boric acid treatment increases the stabilisation rate creating additional benefits for the carbon fibre production besides the increase in carbon yield and the reduction of gas emission.

5. ACKNOWLEDGEMENTS:

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6. REFERENCES:

Bacon R, Tang MM (1964) Carbonization of cellulose fibers-II. Physical property study. Carbon N Y 2:221–225. https://doi.org/10.1016/0008-6223(64)90036-3

Baker FS (2010) Low Cost Carbon Fiber from Renewable Resources. In: U.S Dep. energy. https://www1.eere.energy.gov/vehiclesandfuels/pdfs/merit_review_2010/lightweight_materials/lm005_baker_2010_o.pdf. Accessed 13 Jul 2020

Bengtsson A, Bengtsson J, Sedin M, Sjöholm E (2019) Carbon Fibers from Lignin-Cellulose Precursors: Effect of Stabilization Conditions. ACS Sustain Chem Eng 7:8440–8448. https://doi.org/10.1021/acssuschemeng.9b00108

Bridgwater A V., Czernik S, Diebold JM, Oasmaa D (1999) A. Fast Pyrolysis of Biomass: A Handbook. CPL Press, Newbury

Byrne N, Chen J, Fox B (2014) Enhancing the carbon yield of cellulose based carbon fibres with ionic liquid impregnates. J Mater Chem A 2:15758–15762. https://doi.org/10.1039/c4ta04059g

Byrne N, De Silva R, Ma Y, et al (2018) Enhanced stabilization of cellulose-lignin hybrid filaments for carbon fiber production. Cellulose 25:723–733.

https://doi.org/10.1007/s10570-017-1579-0

Byrne N, Setty M, Blight S, et al (2016) Cellulose-Derived Carbon Fibers Produced via a Continuous Carbonization Process: Investigating Precursor Choice and Carbonization Conditions. Macromol Chem Phys 217:2517–2524. https://doi.org/10.1002/macp.201600236

Choi D, Kil HS, Lee S (2019) Fabrication of low-cost carbon fibers using economical precursors and advanced processing technologies. Carbon N Y 142:610–649. https://doi.org/10.1016/j.carbon.2018.10.028

Di Blasi C, Branca C, Galgano A (2007) Flame retarding of wood by impregnation with boric acid - Pyrolysis products and char oxidation rates. Polym Degrad Stab 92:752–764. https://doi.org/10.1016/j.polymdegradstab.2007.02.007

Downing M (2013) DOE Lignin to Carbon Fiber Workshop. In: U.S Dep. energy. http://www1.eere.energy.gov/bioenergy/pdfs/carbon_fiber_workshop_downing.pdf. Accessed 6 Apr 2020

Ford CE, Mitchell C V. (1963) Fibrous graphite. US Pat. 3,107,152 1–5

Frank E, Steudle LM, Ingildeev D, et al (2014) Carbon fibers: Precursor systems, processing, structure, and properties. Angew Chemie - Int Ed 53:5262–5298. https://doi.org/10.1002/anie.201306129

Jagtoyen M, Derbyshire F (1998) Activated carbons from yellow poplar and white oak by H3PO4 activation. Carbon N Y 36:1085–1097. https://doi.org/10.1016/S0008-6223(98)00082-7

Kandola BK, Horrocks AR, Price D, Coleman G V (1996) Flame-Retardant Treatments of Cellulose and Their Influence on the Mechanism of Cellulose Pyrolysis. J Macromol Sci Part C 36:721–794. https://doi.org/10.1080/15321799608014859

Karacan I, Soy T (2013) Enhancement of oxidative stabilization of viscose rayon fibers impregnated with ammonium sulfate prior to carbonization and activation steps. J Appl Polym Sci 128:1239–1249. https://doi.org/10.1002/app.38496

Kozłowski RM, Muzyczek M (2020) 10 - Improving the flame retardancy of natural fibres. In: The Textile Institute Book Series. Woodhead Publishing, pp 355–391

LEVAN SL (1984) Chemistry of Fire Retardancy. In: The Chemistry of Solid Wood. American Chemical Society, pp 531–574

LeVan SL, Tran HC (1990) The role of boron in flame-retardant treatments. In: First International Conference on Wood Protection with Diffusible Preservatives. Forest Products Research Society, Nashville, TN, Madison, WI, pp 39–41

Lewin M (1985) Handbook of Fiber Science and Technology Volume 2 : Chemical Processing of Fibers and Fabrics - Functional Finishes. Marcel Dekker, Inc, New York,NY

Li S, Lyons-Hart J, Banyasz J, Shafer K (2001) Real-time evolved gas analysis by FTIR method: An experimental study of cellulose pyrolysis. Fuel 80:1809–1817. https://doi.org/10.1016/S0016-2361(01)00064-3

Ma Y, Asaadi S, Johansson L-S, et al (2015) High-Strength Composite Fibers from Cellulose-Lignin Blends Regenerated from Ionic Liquid Solution. ChemSusChem 8:4030–4039. https://doi.org/10.1002/cssc.201501094

Morgan P (2005) Carbon Fibers and Their Composites. CRC Press, Boca Raton

Morrey EL (2003) Flame retardant composite materials: Measurement and modelling of ignition properties. In: Journal of Thermal Analysis and Calorimetry. pp 943–954

Ogale AA, Zhang M, Jin J (2016) Recent advances in carbon fibers derived from biobased precursors. J Appl Polym Sci 133:. https://doi.org/10.1002/app.43794

Olsson C, Sjöholm E, Reimann A (2017) Carbon fibres from precursors produced by dry-jet wet-spinning of kraft lignin blended with kraft pulps. Holzforschung 71:275–283. https://doi.org/10.1515/hf-2016-0189

Pappin B, J. M, A. T (2012) Boron-Carbohydrate Interactions. In: Carbohydrates - Comprehensive Studies on Glycobiology and Glycotechnology. InTech, Rijeka

Peak D, Luther G, Sparks D (2003) ATR-FTIR Spectroscopic Studies of Boric Acid Adsorption on Hydrous Ferric Oxide. Geochim Cosmochim Acta 67:2551–2560. https://doi.org/10.1016/S0016-7037(03)00096-6

Romanos J, Beckner M, Stalla D, et al (2013) Infrared study of boron-carbon chemical bonds in boron-doped activated carbon. Carbon N Y 54:208. https://doi.org/10.1016/j.carbon.2012.11.031

Roth M, Schwarzinger C, Mueller U, Schmidt H (2007) Determination of reaction mechanisms and evaluation of flame retardants in wood-melamine resin-composites. J Anal Appl Pyrolysis 79:306–312. https://doi.org/10.1016/j.jaap.2006.10.002

Schuyten HA, Weaver JW, Reid JD (1955) Effect of Flameproofing Agents on Cotton Cellulose. Ind Eng Chem 47:1433–1439. https://doi.org/10.1021/ie50547a049

Shawgi N, Li SX, Wang S (2017) A Novel method of synthesis of high purity nano plated boron carbide powder by a solid-state reaction of poly (vinyl alcohol) and boric acid. Ceram Int 43:10554–10558. https://doi.org/10.1016/j.ceramint.2017.05.120

Strong SL (1974) Small-scale heat-treatment of rayon precursors for stress-graphitization. J

Mater Sci 9:993–1003. https://doi.org/10.1007/BF00570395

Weser U (2008) Chemistry and structure of some borate polyol compounds of biochemical interest. In: Structure and Bonding. Springer Berlin Heidelberg, pp 160–180

Yang H, Yan R, Chen H, et al (2007) Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 86:1781–1788. https://doi.org/10.1016/j.fuel.2006.12.013

Zhang Y, Zhang W, Lu W (2016) Effect on tensile strength of wood-based carbon fiber impregnated by boron. BioResources 11:5075–5082. https://doi.org/10.15376/biores.11.2.5075-5082