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Accelerating the formation of the conjugated ladder structure of Poly (acrylonitrile-co-vinyl acetate) by cross-linked poplar lignin doped with boron phosphate

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Abstract

Utilizing renewable resources and accelerating thermal stabilization have been two main effective technical means to reduce the cost of poly(acrylonitrile) (PAN) based carbon fibre (CF). In this work, cross-linked poplar lignin (CPPL) with higher carbon content and 15 times the weight-average molecular weight of poplar lignin (PPL) was formed by doping boron phosphate (BP) in situ composites, which was blended with poly(acrylonitrile-co-vinyl acetate) (PANVA) to prepare a low-cost partially bio-based composite PANVA/CPPL-BP. During thermal stabilization, the C1s curve-fitting of x-ray photoelectron spectroscopy (XPS) spectra showed that the conjugated ladder structure of PANVA/CPPL-BP started to form at 230 °C, which was 20 °C lower than PANVA. And the acceleration in forming conjugated ladder structures was further confirmed by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric (TG), and TG-FTIR. During simulated low-temperature carbonization for composites stabilized at 230 °C in advance, the addition of CPPL-BP greatly improved the order of graphitic structure for PANVA. The mechanical property of CF mats has also been obviously improved by CPPL-BP. The possible mechanism that CPPL-BP accelerating the formation of conjugated ladder structures for PANVA/CPPL-BP during thermal stabilization was proposed. With such improvement on accelerating thermal stabilization and utilizing cheap bio-material at the same time, this PANVA/CPPL-BP composite has a great potential in developing low-cost CF.

1. Introduction

PAN has been the dominant CF precursor—the raw material used to make CF, accounting for over 90% of the commercial CF precursor [1]. CF is a light-weight material with excellent mechanical properties used in both structural and non-structural applications. However, the high cost of commercial CFs (about US$25.7/kg) is the barrier for its widespread application. And the cost of precursor occupies more than 50% of the cost of CF [2, 3]. Thus, utilizing low-cost renewable resources as CF precursor has become a hot spot of current research to expand the application of CF. Moreover, in conversion of PAN to CF, thermal stabilization takes over 65% of the total energy of conversion [4]. Besides, thermal stabilization takes up to 1120 min for PAN/lignin blends [5] and up to 4530 min for lignin [6]. Therefore, saving energy from thermal stabilization is also required to satisfy the huge demand of low-cost CF.
Lignin is the second most abundant available biopolymer with branched polyphenolic network structures on the earth, which is commonly extracted as a by-product in paper and pulp industries by 70 million tons annually [7, 8]. The carbon content of lignin is over 60% according to its three main structure units, including syringyl (S), guaiacyl (G) and p-hydroxyphenyl (H) units [9, 10]. And the cost of lignin is only US$1.1/kg [11], which is much cheaper than PAN. It makes lignin as a potential precursor for low-cost CF in non-structural applications [2, 12, 13]. Recently, blending lignin with PAN has been considered as an relatively inexpensive and convenient approach to reduce the overall cost of CF fabricating [14, 15].

Thermal stabilization is a prerequisite process in PAN-based CFs production, during which linear PAN chain transfers into conjugated ladder structure mainly through cyclization and dehydrogenation for PAN to be thermal stable in subsequent carbonization process [16, 17]. Hence, accelerating the formation of conjugated ladder structures is the key to accelerate thermal stabilization. Inspired by BP catalysing dehydrogenation, dehydration and aromatization to form a more compact char layer due to Bronsted and Lewis acid sites [18], utilizing this low-cost, non-toxic and active char-forming catalyst may be beneficial to accelerate the formation of conjugated ladder structures. Boron acid and phosphorus compounds have been introduced to catalyse the formation of ordered carbon structure thus increase mechanical properties [2, 19, 20]. Besides, The oxygen-bearing groups in lignin and BP may provide more possibilities for oxygen-induced dehydrogenation and nucleophilic attack to C≡N of PAN to initiate cyclization. In addition, we speculate that BP could catalyse the formation of cross-linked structure and unsaturated bond through dehydrogenation and dehydrogenation of PPL respectively, which increases the molecular weight and carbon content of PPL, making it more promising to apply lignin as CF precursor.

Studying the formation of conjugated ladder structures which consists of condensed six-member conjugated rings is the theoretical basis to understand the structural evolution during thermal stabilization. XPS analysis has been commonly used on surface characterization since 1980s [21], because it is sensitive to surface conditions and not disturbed by intense photon absorption, and not only element composition but also chemical state can be obtained by XPS [21–23]. Here, the curve-fitting of C1s XPS spectra can provide structural composition of different carbon states. Therefore, applying C1s XPS spectra to study the formation of conjugated ladder structures at different temperatures will give a better understanding of lignin and BP affecting the structural evolution during thermal stabilization and provide a suitable temperature for this procedure.

In this work, a partially bio-based composite PANVA/CPPL-BP was prepared. XPS was applied to investigate the structural evolution of the composites during thermal stabilization under different temperatures, which was supplemented by 31P NMR, GPC, FTIR, DSC, TG, TG-FTIR and Raman analysis. And the possible mechanism of CPPL-BP catalysing the formation of conjugated ladder structures of PANVA was discussed.

2. Materials and methods

2.1. Materials

Poly(acrylonitrile-co-vinyl acetate) copolymer (PANVA) (Mw = 38.73 × 10⁴ g mol⁻¹, the addition of vinyl acetate is 3%) and poplar lignin (PPL) (Mw = 5.26 × 10⁴ g mol⁻¹, purity is 98.0%, and carbon content is 60.5%) were both supplied by Ningbo Institute of Material Technology & Engineering, Chinese Academy of Science. Boron phosphate (BP) powder was prepared from boric acid and phosphoric acid according to previous work [24]. The calcination temperature was 500 °C and the molar ratio of boron and phosphorus was 1:25. Dimethyl sulfoxide (DMSO, Beijing Tongguang Fine Chemical Company) was analytically pure and used as received.

2.2. Preparation of PANVA/CPPL-BP composite

PANVA/CPPL-BP was prepared by doping BP in situ in DMSO solution of PANVA/PPL at 70 °C under stirring for 4 h at a total mixture concentration of 10 wt%. PANVA and PPL was in the weight ratio of 2/1, and the concentration of BP was 1 wt%. To study the mechanism of the structural evolution, PANVA, PANVA/PPL (7/3 wt%), PANVA/CPPL-BP (BP: 1 wt%) and CPPL-BP (BP: 1 wt%) solution with exactly the same concentration (10 wt%) in DMSO were also prepared at 70 °C under stirring for 4 h. 0.5 mL of solution was dropwise added on aluminium foil which was fixed on spin coater KW-4A (Institute of Microelectronics of Chinese Academy of Sciences), and spun at the rate of 500 rpm for 30 s and then 1500 rpm for 30 s. Then, all the films (2 × 2 cm²) were prepared after completely dried in vacuum oven at 60 °C for 24 h. Thermal stabilization was carried out under air atmosphere using tube furnace OTF-1200× (Hefei Kejing material technology Co., Ltd). And the heating rate was 5 °C/min from 30 °C to target temperatures (200 °C, 230 °C, 240 °C, 250 °C, 260 °C, 270 °C, 300 °C, respectively), then stabilized samples were prepared after being kept at the target temperatures for 60 min.
2.3. Preparation of carbon fibre mat
Electrospinning was used to fabricate the PANVA, PANVA/PPL and PANVA/CPPL-BP fibre mats. The applied voltage was 20 kV, the working distance was 15 cm, and the feeding rate was 0.0010 mm/s. The as-spun fibre was stabilized at 230 °C then carbonized at 700 °C as the stabilization and carbonization processes mentioned above. The obtained PANVA_stabl. CF mat, PANVA/PPL_stabl. CF mat and PANVA/CPPL-BP_stabl. CF mat were named as CFs-1, CFs-2 and CFs-3.

2.4. Characterization
XPS was applied to study the Brønsted and Lewis acid sites of BP, and ethylenediamine was used as a probe according to the published detailed procedure [25]. XPS was also used to analyze carbon atom chemical state of CPPL-BP and the formation of conjugated ladder structures of samples at different temperatures during thermal stabilization. XPS data were obtained on PHI Quantera II SXM (Ulvac-Phi, Inc., Japan). Al Kα (1486.7 eV) was applied as x-ray source under a power of 25 W (15 kV). The beam spot is 100 μm, x-ray incident angle is 45° and vacuum pressure is about 10⁻⁸ Pa. High resolution XPS spectra for elements were obtained after 6 times of scanning. ³¹P NMR spectroscopy was used to analyse hydroxyl groups of PPL at room temperature on Bruker Ascend 400 M (Bruker, U.S.). Here, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) reacts with hydroxyl groups of lignin to give phosphitylated products, and N-hydroxy-5-norbornene-2,3-dicarboximide was used as internal standard [26, 27]. Gel permeation chromatography (GPC) was applied to analyse the molecular weight of CPPL-BP and PPL on HLC 8320 (Tosoh, Japan). For GPC, the mobile phase was DMF/LiBr, the temperature was 40 °C, the injection concentration was 0.2%, and the injection flow rate was 0.6 mL per minute. FTIR spectra was used to follow the structural evolution of samples. It was recorded on Nicolet 6700 FTIR spectrometer (Thermo Nicolet Corporation, U.S.) in the range of 4000-400 cm⁻¹, with 32 scans at a resolution of 4 cm⁻¹, and the coordinate of all spectra were normalized. Thermal events were investigated through differential scanning calorimetry (DSC), which was conducted on Q20 (TA Instruments, U.S.) at a heating rate of 10 °C/min under N₂ atmosphere. Thermal property was studied by thermogravimetric (TG) analysis, which was performed on Netzsch 209 F1 thermal analyser (Netzsch Instruments, Germany) at a heating rate of 10 °C/min under N₂ atmosphere. The calculated TG curve of PANVA/PPL was summed up as following [28]:

\[ W_{\text{Cat}}(T) = \sum_{i=1}^{n} x_i W_i(T) \]  

where \( T \) is the temperature, \( x_i \) is the content of compound \( i \) and \( W_i \) is the weight of compound \( i \). TG was coupled with FTIR (TG-FTIR) to track the evolved gas during TG analysis. Raman spectra was performed to study the graphic structure, which was recorded on inVia Raman Microscope (Renishaw plc, UK) with a laser excitation wavelength of 532 nm, and the scan range is 750–2000 cm⁻¹. Scanning Electron Microscope (SEM) was used to obtain the micromorphology of CF on Hitachi S-4800. The mechanical property of the CF mats was performed through a tensile tester (H50K-S UTM, UK) at a strain rate of 2 mm/min. The testing size of the CF mats was 20 mm × 4 mm.

3. Results and discussion

3.1. Formation of cross-linked PPL-BP by doping BP in situ
To confirm the cross-linking of PPL doped with BP, the structures and molecular weight of CPPL-BP and PPL are analysed. Owing to that Brønsted and Lewis acid sites of BP (figure S1) can catalyse dehydration of the hydroxyl groups (figures S2 and S3 is available online at stacks.iop.org/MRX/7/055309/mmedia) and dehydrogenation of lignin, the hydroxyl groups formed into C=C bond, C=O–C bond and C=O bond as in figure 1(a). From figure 1(b), the weight-average molecular weight of CPPL-BP is 15 times of PPL after doping BP in situ, which evidently confirmed the cross-linking of PPL. In FTIR spectra (figure 1(c)), the absorption peaks of \( \text{C}=\text{O} (1720 \text{ cm}^{-1}), \text{C}=\text{O}–\text{C} (1032 \text{ cm}^{-1}) \) [29] and \( \text{C}=\text{C}–\text{H} (951 \text{ cm}^{-1}) \) [30] stretching in CPPL-BP are stronger than PPL. And in curve-fitting of C1s XPS spectra (figures 2(a) and (b)), the content of aliphatic C (C–C, C=C) increases and the content of C–O decreases. It also indicates the formation of CPPL-BP which contains more unsaturated bonds. Thus, the CPPL-BP is formed by doping BP in situ. Besides, the relative carbon content of CPPL-BP is 83.9% (figure S4), 6.9% higher than PPL, which is with more prospect as CF precursor.

3.2. Formation of conjugated ladder structures in air
High resolution C1s XPS spectra are recorded to analyse the chemical state of carbon atom to observe the formation of conjugated ladder structures for PANVA and its composites during thermal stabilization. C1s spectra of samples at different temperatures during thermal stabilization are fitted in figures 4–6 according to the
peak assignment and chemical shift relative to benzene-like C in table 1, and the structure of benzene-like C is shown in figure 3. The curve-fitting results can be seen in tables S1-S3. When temperature increases, different carbon states change gradually in the fitted C1s XPS spectra. The carbon in conjugated ladder structure can be defined as benzene-like carbon at the binding energy of 284.4 eV. Firstly, benzene-like carbon appears and the content of C≡N decreases when conjugated ladder structure is formed due to dehydrogenation and cyclization. For PANVA, the content of C≡N starts to decrease at 240 °C, and the content of benzene-like carbon is 6.55% at 240 °C and increases greatly to 19.11% at 250 °C. And 250 °C is normally applied as the temperature of thermal stabilization for PANVA. While in PANVA/PPL, the benzene-like carbon at R.T. (room temperature) is originated from benzene ring of PPL. The content of C≡N starts to decrease at 230 °C, and the content of
benzene-like carbon gains 4.18% at 230 °C then increases evidently to 23.87% at 240 °C. It’s worth noting that, after doping 1 wt% of BP into PPL, the content of benzene-like carbon efficiently increases to 23.18% (gains 14.60%) at 230 °C for PANVA/CPPL-BP, and the highest content of benzene-like carbon from conjugated
ladder structure is achieved in PANVA/CPPL-BP at each temperature. It reveals that cyclization is more effectively initiated by CPPL-BP, and the thermal stabilization of PANIA/CPPL-BP can carry out at 230 °C, which is 20 °C lower than PANVA.

The other evidence of conjugated ladder structure lies in π–π* shake-up and ‘asymmetric tailing’ (the baseline of high binding energy side is higher than low binding energy side) in C1s curve-fitting. After an electron is emitted during the photoionization process, valence electron will rearrange. When the conjugated ladder structure is formed, the valence electron from the highest occupied molecular orbital (HOMO) probably transits to an unoccupied lowest unoccupied molecular orbital (LUMO) [35], resulting in π–π* shake-up [36]. Besides, the gap to Femi energy level also decreases [37], so that multi valence electrons can transit to empty states in Femi energy level, which leads to asymmetric tailing. For PANVA, π–π* shake-up and ‘asymmetric tailing’ both become stronger after 250 °C. By comparison, π–π* shake-up and ‘asymmetric tailing’ slightly exist in PANVA/PPL and PANVA/CPPL-BP since 200 °C due to the benzene ring of PPL and then enhanced evidently after 230 °C because of the formation of conjugated ladder structures. From above results, PANVA/CPPL-BP composite shows the significantly increase of content of benzene-like carbon, appearance of π–π* shake-up and ‘asymmetric tailing’ in C1s curve-fitting at 230 °C, due to the formation of conjugated ladder structures accelerated by CPPL-BP.

FTIR spectra (figures 7(a)–(c)) of PANVA, PANVA/PPL and PANVA/CPPL-BP under different temperatures during thermal stabilization also provide proof of acceleration in cyclization and dehydrogenation. When temperature increases for these three systems, the intensity of peak at 2243 cm\(^{-1}\) (C≡N band) decreases due to cyclization, and the intensity of peak at 1596 cm\(^{-1}\) (C=N band and C=C band) [38, 39].
increases because of cyclization and dehydrogenation. For PANVA, the peak at 1596 cm\(^{-1}\) originated from C\(=\)C band is strengthened at 230\(^{\circ}\)C when the peak at 2243 cm\(^{-1}\) doesn’t change, which indicates that dehydrogenation occurs at 230\(^{\circ}\)C. The peak at 2243 cm\(^{-1}\) starts to decrease at 240\(^{\circ}\)C owing to cyclization which becomes evident at 250\(^{\circ}\)C. By comparison, cyclization and dehydrogenation for PANVA/PPL and PANVA/CPPL-BP are both accelerated since 230\(^{\circ}\)C.

3.3. Analysis of cyclization and dehydrogenation in nitrogen

In nitrogen atmosphere, the influence of oxygen is removed, and the effect of oxygen-bearing groups of CPPL-BP on PANVA are clearer to analyse. As DSC curves illustrated in figure 8(a), the exothermic peak of PANVA at 312.4 \(^{\circ}\)C corresponds to cyclization of C≡N [1]. The peak temperature of PANVA/PPL and PANVA/CPPL-BP greatly decreases to 294.9 \(^{\circ}\)C and 294.1 \(^{\circ}\)C, respectively. But the released heat of PANVA/PPL (83.9 J g\(^{-1}\)) is higher than PANVA (69.6 J g\(^{-1}\)), which probably increases the risk of breaking molecular chains and causing defects [40]. Notably, the released heat of PANVA/CPPL-BP is reduced to 63.9 J g\(^{-1}\), which is equivalent to 23.8\% reduction from PANVA/PPL. Figure 8(b) illustrates the TG curves under N\(_2\) atmosphere and table 2.

Table 2. Residue of samples from TG analysis.

| Sample       | Residue\(_{700 \, ^{\circ}\text{C}}\) (%) |
|--------------|-----------------------------------------|
|              | Exp./Cal.                              | Interactional efficiency$^*$ |
| PANVA        | 32.2/—                                 | —                          |
| PPL          | 42.6/—                                 | —                          |
| PANVA/PPL    | 55.5/35.3                               | 0.7 (PPL)                  |
| PANVA/CPPL-BP| 44.2/32.9                               | 11.3 (BP)                  |

$^*$ Interactional efficiency: the increase value from Cal. to Exp. residue for one percentage of PPL and BP, respectively. And BP hardly has degradation under 700 \(^{\circ}\)C [18, 41].

Mater. Res. Express 7 (2020) 055309 H Shi et al.
shows the residue values and the interactional efficiency for samples at 700 °C. The increase from the calculated (Cal.) residue value to the experimental (Exp.) residue value reveals that PPL and BP both have interaction effect with PANVA on formation of thermal stable structure, and the results present that BP has comparably higher interactional efficiency than PPL. Besides, in the 3D FTIR spectra (figures 8(c) and (d)) during TG-FTIR analysis under N₂ atmosphere, H₂O is released at lower temperature in PANVA/BP than PANVA, which indicates that oxygen-induced dehydrogenation of PANVA is accelerated by BP to form thermal stable structure.

From above results, it suggests that CPPL-BP can initiate cyclization, and PPL and BP both have interaction effect with PANVA to finally form thermal stable structure. Therefore, the acceleration in forming conjugated ladder structure of PANVA/CPPL-BP by CPPL-BP is further confirmed.

3.4. Possible mechanism of forming conjugated ladder structure
Based on the analysis above, a possible mechanism of CPPL-BP accelerating the formation of conjugated ladder structures is proposed as in figure 9. Cross-linked PPL-BP was prepared by doping BP in situ composites of PANVA/PPL, which increases the carbon content and weight-average molecular weight of PPL by intermolecular dehydration. For PANVA, cyclization and dehydrogenation are two main reactions to transfer the linear structure into conjugated ladder structure. For PANVA/CPPL-BP, on one side, CPPL-BP provides oxygen for the oxygen-induced dehydrogenation, which is catalysed by Brønsted and Lewis acid sites of BP at the same time. On the other side, cyclization of C≡N can be greatly initiated at a lower temperature through nucleophilic attack by negative charge centres from CPPL-BP. Thus, the formation of conjugated ladder
structures is accelerated, making it possible to carry out thermal stabilization at a lower temperature, which is promising to reduce the cost and save energy.

3.5. Simulating low-temperature carbonization

Considering the formation of conjugated ladder structures is accelerated by PPL and CPPL-BP at 230 °C during thermal stabilization, PANVA_stabl., PANVA/PPL_stabl. and PANVA/CPPL-BP_stabl. which are stabilized at 230 °C are subsequently carbonized in TG analysis up to 700 °C under N2 atmosphere simulating low-temperature carbonization. In figure 10(a), the residues don’t have much differences, which indicates that stabilization under 230 °C ensures the thermal stability. Moreover, Raman spectrum for sample char from TG analysis at 700 °C (figure 10(b)) provides insight into the carbonaceous structure. D band at 1348 cm⁻¹ and G band at 1580 cm⁻¹ correspond to disordered and ordered graphitic structure, respectively [42, 43]. The lowest ID/IG value of char-3 from PANVA/CPPL-BP_stabl. relates to its highest ordered graphitic structure. Thus, it confirms that PANVA/CPPL-BP_stabl. with the conjugated ladder structure formed at 230 °C during thermal stabilization can generate higher ordered graphitic structure in subsequent low-temperature carbonization.

3.6. Mechanical property of carbonized fibre mat

The histogram results of mechanical property for CFs-1, CFs-2 and CFs-3 are shown in figure 11. The tensile stress of the samples is calculated by the following equations (2) and (3):

\[
\text{stress (N/Tex)} = \frac{[\text{force (N)/width (mm)}]}{\text{areal density (g/m}^2\text{)}} \quad (2)
\]

\[
\text{tensile stress (GPa)} = \text{stress (N/Tex)} \times \text{density (g/cm}^3\text{)} \quad (3)
\]

The areal density is the weight divided by its area, and the tensile stress is calculated from stress by multiplying the density of the sample. By comparing these three samples, CFs-2 has the lowest tensile stress, but
CFs-3 has the highest tensile stress. And the strain at break decreases from CFs-1 (0.93%) to CFs-2 (0.45%), while the value of CFs-3 increases to 0.72%. This may due to that the molecular weight of PPL is too low which decreases the tensile stress and strain at break even though PPL has interaction effect with PANVA on forming thermal stable structure. While the molecular weight of CPPL-BP and the interactional efficiency of BP are both much higher than PPL, thus significantly improves the mechanical properties for CFs-3.

4. Conclusions

In this paper, CPPL-BP with 15 times the weight-average molecular weight of PPL by doping BP in situ was made, and the content of unsaturated carbon increases for CPPL-BP owing to the dehydrogenation and dehydrogenation. The formation of conjugated ladder structures during thermal stabilization was greatly accelerated at 230 °C for PANVA/CPPL-BP composites, which was 20 °C earlier than PANVA. And the dehydrogenation and cyclization induced by CPPL-BP were also confirmed. BP shows much higher efficiency with PANVA on formation of thermal stable structure than PPL. The mechanism of CPPL-BP accelerating the formation of conjugated ladder structures for composites was proposed based on the oxygen-induced dehydrogenation and cyclization of PANVA. It revealed that CPPL-BP provided oxygen for the oxygen-induced dehydrogenation, which was catalysed by Lewis and Brønsted acid sites of BP. In addition, negative charge centres of CPPL-BP initiated cyclization of C≡N at a lower temperature. PANVA/CPPL-BP stabilised at 230 °C in air showed the highest ordered graphitic structure. Besides, CPPL-BP significantly improves the tensile stress and strain at break of CF mats. The application of cross-linked PPL doped with BP in this study significantly accelerated thermal stabilization, suggesting an effective method to not only reduce the cost of precursor but also save energy from thermal stabilization for fabricating partially bio-based low-cost CF.

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