PREPARATION OF COST-COMPETITIVE ISOTROPIC PITCH PRECURSORS FOR CARBON FIBER THROUGH A MODIFIED OXIDATIVE THERMAL TREATMENT OF PETROLEUM RESIDUE

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Introduction

Carbon fibers are considered one of the strongest candidates to replace conventional steel-based materials due to their outstanding mechanical properties while light weights. But the biggest impediment to expanding their application area is the high production cost[1-6]. Herein, we introduce a modified oxidative thermal treatment as a cost-competitive way to produce spinnable isotropic pitch from petroleum residue. Pyrolysis fuel oil (PFO) was used as a starting petroleum residue, and it was thermally treated under the presence of O_2/N_2 mixed gas. The effects on softening point, pitch yield, and spinnability were investigated with varying O_2 concentration from 0% to 50%.

Materials and Methods

Pyrolysis fuel oil, so called PFO, was used as the starting material to synthesize pitch precursor. In a typical process, 700 g of PFO was added to a 1 L reactor and heat treated at 360 °C for 5 h under vigorous agitation along with O_2-containing reaction gas blown at a flow rate of 0.5 L/min. Using this method, two series of pitch were prepared. First, the O_2 concentration in the reaction gas was set to 0%, 20%, 35% or 50% by volume to produce a series of pitches labeled POx-00, POx-20, POx-35 and POx-50, respectively. Another series of pitch was prepared by setting the flow rate of the reaction gas to 0.7, 1.0 and 2.0 L/min at a fixed O_2 concentration of 20%.
The resultant pitch precursors were analyzed via MALDI-TOF-MS, FTIR, and ^{1}H- and ^{13}C-NMR. Carbon fibers were also prepared from the pitch precursors through melt-spinning and subsequent heat-treatments of stabilization (210 °C for 15h) and carbonization (1100 °C for 1h).

Results and Discussion

Figure 1(a) shows that the conventional air-blowing method increased softening point of isotropic pitches from 209 °C to 282 °C through adjusting the air flow rate, but which accompanied rapid decrease in pitch yield from 33.1% to 24.6% (–8.5%). In contrast, the modified oxidative thermal treatment presented in this study effectively suppressed the decrease in pitch yield. Figure 1(b) shows that pitch yield was kept constant at 33% when softening point was increased from 130 to 280 °C. This is because of facilitation of condensation reactions between constituting polyaromatic hydrocarbons and suppression of volatilization of light components during pitch synthesis.
Thus-prepared pitch samples were melt-spun showing good spinnabilities. After the carbonization, comprehensive single filament tensile testings were conducted. The results are depicted in Fig. 2. Carbon fibers prepared from POx-35, POx-20-F07 and POx-20-F10 exhibited tensile strengths of

0.76, 0.82 and 0.81 GPa, which were comparable to that of the control (SN-270-derived carbon fiber, 0.83 GPa). In case of POx-50-derived carbon fiber, the average fiber diameters was relatively larger due to its large amount of quinolone insoluble (QI), and consequently, they showed very low tensile strength (0.47 GPa).

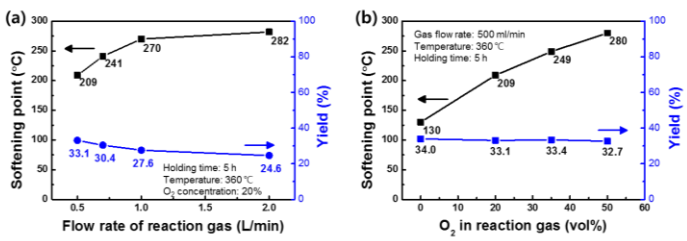

Figure 2. Softening point and yield variation of pitches prepared by oxidative thermal treatment as a function of (a) flow rate of the reaction gas and (b) O_2 concentration in the reaction gas.

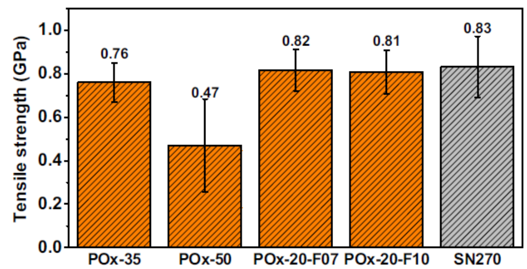

Figure 1. Tensile strength of carbon fibers prepared from the experimental pitch samples (POx-35, POx-50, POx-20-F07 and POx-20-F10) and commercial isotropic pitch (SN- 270).

Conclusions

The modified oxidative thermal treatment was highly effective at increasing the softening point while maintaining high pitch yield. The experimental pitches showed excellent spinnabilites, and the resultant carbon fiber showed moderate mechanical properties. In conclusion, the current research demonstrated that the modified oxidative thermal treatment can be used as a cost-saving method to adjust the softening point of petroleum pitches for low-cost carbon fiber production

Acknowledgment

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