DOI 10.1007/s12182-013-0310-5

Synthesis of condensed polynuclear aromatic resin from furfural extract oil of reduced-pressure route II

Wu Mingbo*, Jiang Wei, Wang Yuwei, Li Shibin and Zheng Jingtang**

State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao, Shandong 266580, China

Abstract: As an industrial byproduct of oil refining, furfural extract oil from reduced-pressure route Ⅱ with high aromatic content was used to prepare heat-resistant condensed polynuclear aromatic (COPNA) resin for the first time. The basic properties of furfural extract oil and the resultant COPNA resin were characterized by infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (^{1}H-NMR), thermogravimetric analysis (TGA) and elemental analysis (EA). The result showed that heat treated furfural extract oil was successfully used for the synthesis of heat-resistant COPNA resin. The average structural parameters of raw materials and prepared resin were calculated by the improved Brown-Ladner method, and the averaged molecular structure of the resin was obtained. The reaction mechanism for the synthesis of COPNA resin was suggested as an acid-catalyzed positive ion type polymerization.

Key words: Furfural extract oil, reduced-pressure route II, COPNA resin, synthesis, reaction mechanism

1 Introduction

The synthesis of COPNA resin was firstly reported by Otani (Otani et al, 1986). As a novel heat-resistant material with good lubricity, mechanical properties and mouldability, this resin has attracted considerable attention for its potential applications (Kusakabe et al, 1998; Li et al, 2010; Lin et al, 2010a; 2010b; Tanemura et al, 2011; 2012; Zhao et al, 2008). In the early stages, raw materials for the preparation of COPNA resin were confined to pure aromatic substances (Nakajima et al, 1995; Nawa, 1996; Nawa and Ohkita, 1997). Recently, a number of similar raw materials including coal derived and petroleum based mixtures have been successfully used to prepare COPNA resin (Guo et al, 2002; Li et al, 2008; Shi et al, 2012; Wu et al, 2012; 2012). Furfural extract oil from reduced-pressure route Ⅱ, commonly used as fuel oil for boilers or for the manufacture of synthetic rubber, is a byproduct of oil refining. With a high aromatic content, narrow molecular weight distribution and low content of heavy metals, furfural extract oil is theoretically considered as an ideal candidate raw material to prepare COPNA resin.

In this work, furfural extract oil from reduced-pressure route Ⅱ was firstly heated at atmospheric pressure to remove its volatile components. Then, COPNA resin was eventually synthesized through the reaction of the thermally condensed oil and the cross-linking agent (1, 4-benzenedimethanol, PXG), which was catalyzed by p-toluene sulfonic acid (PTS). The resultant resin as well as the raw materials were characterized by elemental analysis (EA), infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (^{1}H-NMR) and thermogravimetric analysis (TGA).

*Corresponding authors. email: wumb@upc.edu.cn;
**Corresponding author. email: jtzheng03@163.com
Received July 11, 2013

2 Experimental

2.1 Raw materials

Furfural extract oil from reduced-pressure route II was provided by Jiangshan Polymer Material Company, China. PXG (AR) and PTS (AR) were both purchased from SINOPHARM Chemical Reagent Company, China. Toluene was obtained from Tianjin Chemical Reagent Company, China. Quinoline was purchased from Tingxin Chemical Reagent Company, China.

2.2 Heat treatment of furfural extract oil from reduced-pressure route II

Furfural extract oil from vacuum second side-cut was added into a reaction kettle equipped with a thermometer and mechanical stirrer. The reaction kettle was heated to 420 °C at 2 °C/min in a nitrogen flow of 50 mL/min and then kept for 3 h. A small amount of the light fraction of furfural extract oil was found to have evaporated after heat treatment and the thermally condensed oil was obtained.

2.3 Preparations of COPNA resin

The thermally condensed oil, PXG and PTS (with a weight ratios of 75:20:5) were fully mixed in a reactor, and then the mixture was stirred and heated in a nitrogen flow of 40 mL/min. The reactor was heated to 130 °C at 5 °C/