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Thermal degradation behavior of carborane-containing phenylethynyl terminated imide systems

Jie Yue [a, b], Yuntao Li [a, b, *], Yan Zhao [c], Dong Xiang [b], Youxun Dai [b]

[a] State Key Lab of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, 610050, China
[b] College of Materials Science and Engineering, Southwest Petroleum University, Chengdu, 610050, China
[c] Department of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing, 100191, China

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ABSTRACT

Carborane-containing imide compound (Carb-PEPA) was synthesized and added into fluorinated phenylethynyl terminated imide oligomer (AFR-PEPA). The thermal degradation of Carb-PEPA was studied by thermogravimetric analyzer coupled with Fourier transform infrared analysis (TG-FTIR), in situ FTIR and pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS). The results show that the Carb-PEPA possesses high char yield in both air and nitrogen due to the formation of B–O bonds in thermal degradation process as identified by TG-FTIR and in situ FTIR. A thermal degradation mechanism for the Carb-PEPA was proposed. The Carb-PEPA crosslinks to form polyimide in the early heating process. Then the degradation of Carb-PEPA happens at higher temperatures, while further degradation could be effectively prevented due to the formation of a protection layer of boron oxide compound. The thermal stabilities of AFR-PEPA and AFR-PEPA containing 15 wt% Carb-PEPA (AFR-PEPA-Carb-15) were also studied by TGA and TG-FTIR. It was observed that AFR-PEPA's residual weight ratios at 800 °C in air and nitrogen increased by 20% and 13.3% respectively with the addition of 15 wt% Carb-PEPA.

1. Introduction

High-temperature polyimides and their composites are widely used in a variety of applications, from electronics to aerospace industries, due to their high thermal stability and excellent mechanical, chemical and electrical properties [1–6]. Compared to other addition-type polyimides such as norbornyl or ethynyl terminated polyimide, the phenylethynyl terminated polyimide exhibits many advantages, such as its environmental stability and high glass transition temperature, so that it became an attractive resin matrix for high-performance aerospace composites [7,8]. However, at high service temperatures, the thermal stability and thermal oxidative stability (TOS) of polymer matrix are always of primary concern. Any thermal decompositions or thermal oxidative degradations could potentially affect their service performance in high temperature applications. Many studies have been carried out to improve thermal stability of polyimide materials over the recent years. The previous work demonstrated that making the polymer structure organic/inorganic hybrid could effectively address the issue [7–11]. Carboranes have received extensive attention for developing carborane-containing polymers due to their rich boron contents and great thermal and chemical stability. The thermal stability of polymers could be greatly enhanced by the incorporation of carboranes into the matrices [12–15].

In our previous studies [9], a novel carborane-containing imide compound Carb-PEPA has been prepared through the reaction between 4-aminopheyl-carborane and PEPA (Fig. 1). The cure kinetics of Carb-PEPA and AFR-PEPA were studied. The Carb-PEPA showed excellent thermal stability and high char yield. Although thermal stability and degradation of phenylethynyl terminated polyimides and carborane-containing polymers have been studied by many researchers [13–28], the effect of carborane groups on the pyrolysis mechanism of carborane-containing phenylethynyl terminated imide oligomer is not clear. Andrea D. A et al. [1] investigated the thermal degradation of high-temperature fluorinated phenylethynyl terminated polyimide and its carbon fiber composite. They found that both polyimide resin and composites experienced thermolysis and modest oxidation during degradation. Meanwhile, polyimide composite possessed a higher thermal stability compared to the neat polyimide resin. Yang T et al. [20] studied the

* Corresponding author. State Key Lab of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, 610050, China.
E-mail address: yuntaoli@swpu.edu.cn (Y. Li).

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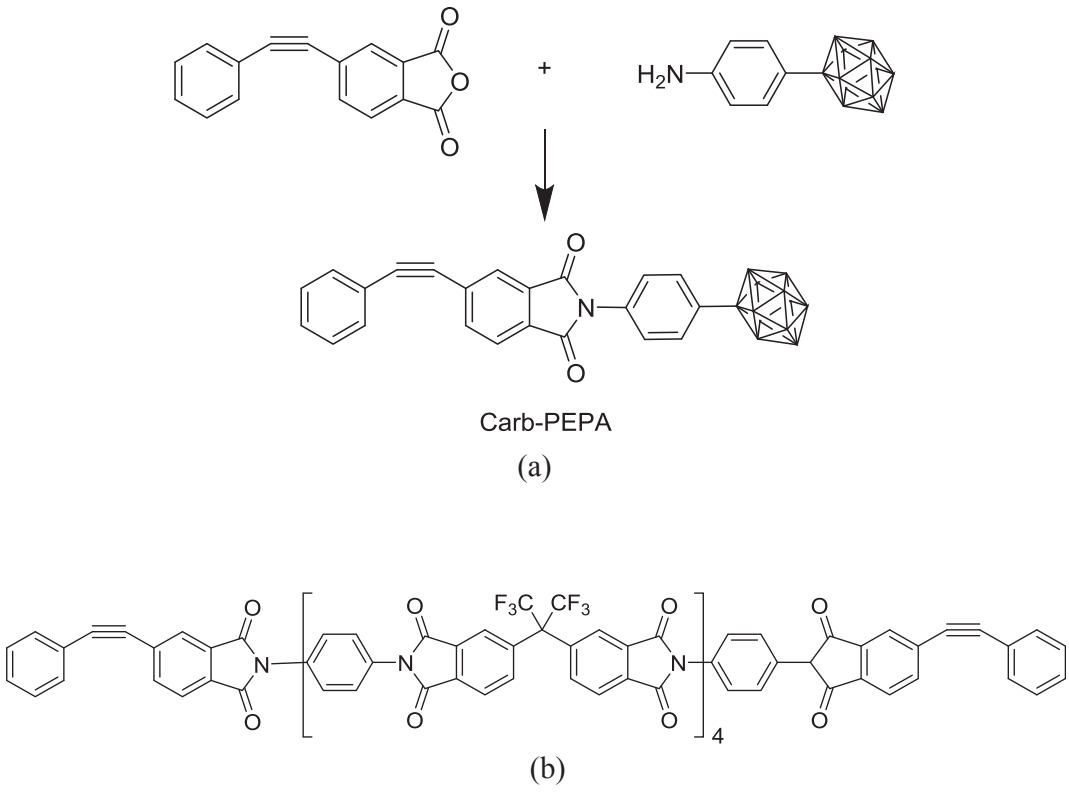

Fig. 1. Chemical structures of the imide compound Carb-PEPA and AFR-PEPA imide oligomer. a. Carb-PEPA; b. AFR-PEPA.

thermal properties of IM7 fibers filled PETI using thermogravimetric analyzer coupled with Fourier transform infrared analysis and mass spectrometry (TG-FTIR-MS). A three-step mechanism for the PETI decomposition was proposed based on the gas evolution. Jiang Y et al. [14] studied the thermal stability and thermal degradation of *o*-carborane-containing poly(siloxane-arylacetylene). It was found that the polymers show excellent thermo oxidative stability with over 85% residue yield at 1000 °C in air.

In this paper, the thermal degradation and pyrolysis behavior of Carb-PEPA are investigated by the evolved gas analysis technique using TG-FTIR and Pyrolysis-GC/MS. A degradation mechanism for the Carb-PEPA is proposed based on the information of decomposition products. In addition, the thermal stability and degradation behavior of the blend of Carb-PEPA and AFR-PEPA was investigated by using TGA and TG-FTIR.

2. Experimental

2.1. Materials

1-(4-aminopheyl)-2-dicarbodeaborane was synthesized according to a reported literature [9]. 4,4′-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 4-phenylethynyl phthalic anhydride (PEPA) were purchased from Changzhou sunlight pharmaceutical. *N*-methylpyrrolidinone (NMP), toluene, 1,4-phenylenediamine (p-PDA) and methanol were provided by Chengdu Kelong Chemical Reagents Corp. (China). Solvents were dried and distilled following the standard procedures. All the reagents were used as received without further purification.

2.2. Synthesis of imide compound Carb-PEPA

The synthesis method of carborane-containing imide compound Carb-PEPA has been reported in our previous work [9]. The 1-(4-aminopheyl)-2-dicarbodeaborane (235 mg, 1 mmol) and PEPA (248 mg, 1 mmol) were dissolved in NMP in a 100 ml round-bottom flask equipped with a magnetic stirrer under the protection of nitrogen atmosphere. The solution was reacted at room temperature for 12 h and then heated up to 140 °C slowly and hold for 12 h. When the reaction was completed, the reaction solution was poured into a petri dish and placed into an oven to remove the NMP to produce powder form material. The resultant powder was dried at 180 °C for 24 h in vacuum. Yield:94%. The imide compound has a theoretical molecular weight of 465.6 g/mol. The chemical structure of Carb-PEPA is shown in Fig. 1a.

2.3. Synthesis of imide oligomer AFR-PEPA

The imide oligomer AFR-PEPA was prepared according to the previous literature [9,21]. The 6FDA (2.2684 g, 10.4 mmol) and p-PDA (1.4068 g, 13 mmol) were dissolved in 60 ml NMP in a 250 ml, three-neck round-bottom flask equipped with a Teflon stirring bar and a gas adaptor in a nitrogen atmosphere at room temperature. The solution was stirred for 20 h at room temperature. Then the solid PEPA (1.2918 g, 5.2 mmol) was added and stirred until completely reacted (4 h) under nitrogen. Subsequently, toluene was added and the resulting mixture was imidized under reflux in an oil bath of 180 °C with the removal of water via azeotropic distillation. The reaction mixtures were finally added into distilled water, filtered, washed in boiling water, followed by the removal of NMP in warm methanol. Very fine yellow powder was produced and dried at 160 °C for 24 h in vacuum. Yield: 96%. The polymerization degree of the imide oligomer is 4 and the theoretical molecular