Preparation of carbon nanomaterials using two-group arc discharge plasma

D.L. Sun [a], R.Y. Hong [a,b,*], J.Y. Liu [a], F. Wang [b], Y.F. Wang [c]

[a] College of Chemistry, Chemical Engineering and Materials Science & State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Soochow University, SIP, Suzhou 215123, China
[b] School of Chemical Engineering, Fuzhou University, Fuzhou 350108, China
[c] NanoComp Co. Ltd., Suzhou SND 215011, China

HIGHLIGHTS

- A new preparation method of carbon materials based on two groups of plasma was achieved.
- One combination of AC arc plasma and DC arc plasma was adopted.
- One combination of non-thermal plasma and thermal plasma was adopted.
- Optimal operation parameters and CB generation mechanism were determined.
- A technical process combined a fluidized bed with plasma system was designed.

GRAPHICAL ABSTRACT
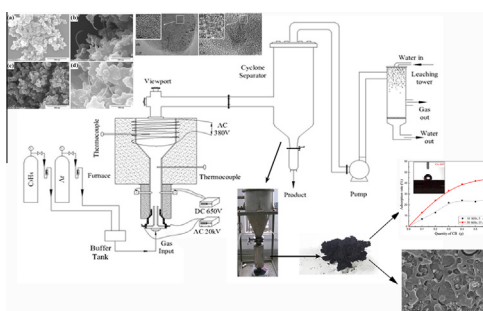
ARTICLE INFO

ABSTRACT

Carbon nanomaterials were prepared using two-group arc discharge plasma method in this study. A combination of an alternating current (AC) arc discharge plasma and a direct current (DC) arc discharge plasma in a fluidized bed was used, in which propane was cracked into carbon blacks (CB) with controlled structure and hydrogen. The effects of parameters such as electrode type, frequency of AC arc discharge, current of DC arc discharge and gas flow ratio (propane/argon) on the synthesis and properties of CB were investigated. A systematic study of the size, morphology, microstructure and surface chemical composition of CB was conducted using various characterization techniques. By using this process, spherical and hydrophobic CB with a narrow size distribution, high degree of graphitization and large specific surface area were produced under optimal experimental conditions. Then, as-prepared CB were used to adsorb heavy-metal ions in water and to reinforce the engineering plastic. The results verified that the adsorption rate of the Cr (VI) ion was increased significantly and that the CB enhanced the electrical and mechanical properties of acrylonitrile–butadiene–styrene (ABS)/natural rubber (NR) composites.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Carbon nanomaterials such as fullerenes, nanotubes, onions, spheres and fibers have been the subject of much research for over two decades due to their excellent physical, chemical and electrical properties [1–3]. These materials have abundant applications as semiconductor materials, hydrogen energy storage media, catalyst

* Corresponding author at: College of Chemistry, Chemical Engineering and Materials Science & State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Soochow University, SIP, Suzhou 215123, China.
   E-mail address: rhong1966@163.com (R.Y. Hong).

supports, composite fillers and reinforcing components [4–7]. Among them, carbon blacks (CB) are one of the most common raw chemical materials and are used as reinforcing filler for rubber goods in tire manufacturing and as pigment for printing inks, coatings and plastics [8,9]. CB are formed by the incomplete combustion of fossil fuels or by thermal decomposition of hydrocarbons, and the formation of CB depends on either the presence or absence of oxygen. Agglomerated primary nanoparticles were obtained from these mechanisms of CB formation [10]. Two growth mechanisms were used to form CB: radial growth and thermal cracking [11,12].

In the industrial production, CB are mainly manufactured using the furnace and channel processes. [13,14]. The furnace process for thermal cracking, which is the predominant method for the production of CB, has been used to meet the demands of the rubber industry for such a long time. This continuous process is operated in a closed reactor and produces a large amount of polluting emissions, including CO_x, SO_x and NO_x. Because energy efficiency and environmental protection have become more important, this technology has an ambiguous future [15]. Therefore, production via plasma has emerged as a potential solution.

In the laboratory, several conventional methods, such as chemical vapor deposition (CVD), laser ablation and arc discharge plasma, have been widely used for preparation of carbon nanomaterials such as CB and carbon nanotubes [16]. However, the CB produced by the CVD method are always contaminated by residual catalytic particles, and the process requires a high operating temperature [17]. Barriers to the commercial adoption of the laser ablation method include its high energy consumption and the fact that it is a non-continuous process. The plasma method is fast and efficient and is widely used at present. Thermal decomposition and plasma systems are more promising than other approaches due to their lower energy consumption [18]. There are two main categories of plasma methods used in materials engineering: thermal plasma and non-thermal plasma. Thermal plasma (thermodynamic equilibrium) is generally operated under high-currents conditions (higher than 1 A). Thermal plasma systems generate plasmas with high temperatures, and all of the systems have the same temperature [11,19]. The thermal plasma concept for CB production has led to the development of "carbon black and hydrogen" using Kvaerner's process [20], and the three-phase arc plasma process by Fulcheri [21]. Additionally, carbon nanostructures can be continuously synthesized using induction thermal plasma technology developed by Soucy and Pristavita [22–26]. The non-thermal plasma (non-thermodynamic equilibrium) approach is generally operated under low current conditions (lower than 1 A), which can provide an electron temperature of 4000–10,000 K and heavy particle temperature of 2000–6000 K. The temperature of these heavy particles (neutrals, ions) can be lower than that of the electrons [11]. The working gas is activated to create highly energetic electrons and reactive species to initiate plasma-assisted chemical reactions [27]. Therefore, non-thermal plasma systems offer highly selective and energy-efficient of chemical reactions.

Numerous researchers have attempted to improve the synthesis of carbon nanomaterials by optimizing conditions and to develop a continuous and large-scale process by using the arc discharge plasma method [28,29]. The plasma methods for the preparation of CB that exist in the current literature are listed in Table 1 [11,13,21,30–39]. However, there are some drawbacks to the conventional arc discharge plasma method that preclude its use in industrial and large-scale applications, such as being a non-continuous process and having poor synthesis purity. On the one hand, there are significant problems to the direct current (DC) discharge method including the necessity of the maintaining the pressure in the reactor below atmospheric pressure and the difficulty of obtaining a large area and uniform discharge. Additionally, in the case of DC arc discharge, carbon vapors aggregate and drift towards the cathode due to the temperature gradient, leading to bridging between the adjacent electrodes. On the other hand, it is still difficult to manufacture massive nano-scale materials by AC arc discharge. From the standpoints of the preparation of CB and of their chemical applications, the thermal discharge process always leads to higher gaseous temperature and has a relatively narrow tolerances for the experimental equipment. However, the gaseous temperature in the conventional non-thermal discharge process is too low for the thermal cracking of a wide range of CB. Therefore, to develop a new approach to overcome these drawbacks, we combined the advantages of both thermal and non-thermal plasma systems by developing powerful discharges, along with a method to control the discharge pattern (AC or DC arc discharge).

In our previous work [34], a non-thermal AC arc discharge plasma method for the preparation of carbon materials has been designed. Here, we demonstrate a promising, large-scale and continuous method for preparing CB. Non-thermal and thermal plasma (AC and DC arc discharge) processes are introduced. Usually, the distance between the electrodes is only 2–3 mm in DC arc discharge [40,41]. Now from a number of onsite tests, the gap between the second pair of electrodes could be as much as 50 mm with the help of the successful arc starter by AC arc discharge. The purposes of this work are (i) to develop an original two-group arc discharge plasma process, based on the establishment of thermal DC discharge at high current–low voltage and non-thermal AC discharge at low current–high voltage, operating at atmospheric pressure for the gas phase synthesis of CB; (ii) to investigate the versatility of the process with respect to the synthesis of carbon nanotubes (CNTs) other than CB; and (iii) to understand CB and CNTs formation mechanisms in such two-group discharge. Previous studies on the decomposition of propane were performed in a fixed or fluidized bed reactor [42,43]. During fluidization, the residence time could be adjusted by changing the rate of the gas flow according to the CB weight. This process was used for the generation of carbon nanomaterials with different structures in a fluidized bed reactor. This work mainly focused on the relationship between the variation of morphology and microstructure of CB and the electrode materials and then developed a description of the formation process of CB.

2. Experimental set-up and procedures

2.1. Materials

Argon (Ar) (purity 99.99%, Jinhong Gas Co., Ltd., China) and propane (C_3H_8) was used as a working gas and carbon source for the preparation of CB, respectively. Two-group parallel electrodes (3 mm and 6 mm in diameter) were used, which were made of different kinds of metals (iron or copper) in the plasma reactor. Natural rubber (NR), recycled acrylonitrile–butadiene–styrene (ABS) and maleic anhydride (MAH) were used.

2.2. Experimental set-up

A schematic of the experimental apparatus is shown in Figs. 1 and 2. The decomposition of C_3H_8 was carried out in a fluidized bed consisting of three sections: an AC arc discharge plasma generator, a DC arc discharge plasma generator and an electric furnace. The functions of the gas (C_3H_8 and Ar) were to replace air that entered the reactor, form plasma for decomposition, completely fluidize the particles and transfer the products. The flow characteristics of CB were calculated and tested in this fluidized bed to determine the minimum fluidized velocity. The temperature in the slim tube and furnace was monitored by two thermocouples installed in two bed positions.