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Catalytic effect of montmorillonite nanoparticles on thermal decomposition of coal tar pitch to carbon

Maciej Gubernat[a,*], Aneta Fraczek-Szczypta[a], Janusz Tomala[b], Stanislaw Blazewicz[a]

[a] AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Al. Mickiewicza 30, 30-059, Cracow, Poland
[b] SGL Carbon Polska S.A., 47-400, Raciborz ul., Piastowska 29, Poland

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ABSTRACT

The work studies the structure of two types of coal tar pitches (CTPs) modified with montmorillonite (MMT) in the form of nanopowder after annealing to 1000 and 2000 °C. The CTPs differed in polycyclic aromatic hydrocarbons (PAH) content and coking value (CV). The study of scanning electron microscope (SEM), transmission electron microscope (TEM) and x-ray diffraction (XRD) showed that the heat treatment of PAH-containing pitches modified with the ceramic filler to 1000 °C is a way to obtain a new clay-carbon nanocomposite, composed of turbostratic carbon, graphitic carbon, carbon nanotubes (CNT) and MMT. MMT act as a catalyst for carbon nanotubes growth *via* the gas phase at 1000 °C. Carbon nanotubes growth in pitch-derived carbon material occurred as a result of the presence of hydrocarbon compounds containing PAH evolved during thermal conversion to the carbon phase. Catalytic growth of carbon nanotubes from aromatic hydrocarbons-containing gaseous phase allows to reduce PAH emission during pitch-derived carbon thermal processing.

The montmorillonite – modified carbon samples contained a graphitic phase built of preferred orientation crystallites. This phase consisted of well-ordered crystallites with the c-axis spacing, d_{002} = 0.335 nm. The process occurred due to catalytic graphitization at 1000 °C in the presence of montmorillonite.

1. Introduction

Coal tar pitches are among the most widely used raw materials in artificial carbon and graphite technologies, including the aluminium and refractory industries, as a binder for electrodes [1]. The pitches are also used as a precursor of carbon for carbon/carbon composites and carbon fibres [2–5]. Among the most important criteria of coal pitches-based binders for carbon products are their appropriate viscosity at moulding temperatures, high coking yield after carbonization, and graphitizability. Coal tar pitches contain polycyclic aromatic hydrocarbons, which are emitted to the environment during their thermal processing [6]. Releasing such substances is highly undesirable due to their toxicity and harmful effect on living organisms and the environment [7]. PAH are characterized by resistance to chemical degradation, proneness to adsorption and bio-accumulation as well as the ability to adhere to particulate matter and contaminate natural and artificial bodies of water [8]. It is the reason why the European Union regulation referring to harmful substances [9] that covers the carbon and graphite industries and their need to reduce PAH release. Thus, there is the need to elaborate new solutions related to raw materials for the carbon and graphite industry. The modification of pitch-derived carbon and graphite materials by using various nanoadditives makes it possible to widen their application to other industrial domains by a specific functionalization of the resulting nanocomposites. Thermal conversion of pitches in the presence of metallic catalysts such as iron or nickel is a well-known method of evoking the catalytic graphitization process [10]. Carbides were also studied for pitches-based carbon modification to form nanocomposites and carbon-ceramic composites [11–15]. The addition of graphene flakes to pitches resulted in an improvement of the graphitic structure of the carbons after heat treatment at 2000 °C [16]. Such a modification evoked an increase of the mechanical parameters and a decrease of the electrical resistivity of the CTP-derived carbon. However, due to the high price of the graphene, its use in industrial-scale production of cathodes is questionable. The effect of carbon nanotubes and graphene flakes on coal tar pitch conversion to graphitic structure has been studied in several works [17–19]. CNT were found to decrease coal tar pitches graphitization ability. Carbon nanotubes are also expensive and are not currently being used at industrial scale as additives to improve the structural ordering of cathodes. A new approach to obtaining such nanocomposites is to force nanotubes growth within the pitch volume during its thermal conversion to graphitic structure. The catalytic growth of carbon nanotubes by the chemical

* Corresponding author.
E-mail address: gubernat@poczta.fm (M. Gubernat).

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vapour deposition (CVD) method can be realized by metallic catalysts such as iron or nickel [20–22]. Moreover, it could be a way to reduce PAH emission during pitches-derived graphite production, by inducing a catalytic CNT growth from the PAH 'carbon precursor' over nickel catalyst [23]. However, the use of metal catalysts for catalytic growth of nanotubes for the fabrication of pure graphite structure can lead to unacceptable contamination of the final product. Various ceramic oxides including MgO, TiO_2, Al_2O_3, and SiO_2, were reported as catalysts of CNT growth and heterogeneous graphitization process [24]. More importantly, these catalysts due to their nonmagnetic properties have advantages during carbon nanotube growth and in the catalytic graphitization, which is important for electronics applications to avoid pitting and contamination [25–30].

Montmorillonite clay is a well-known and cheap material, widely applied to polymers as a flame-retardant nanocomponent [31–33]. Clay–carbon composites have also been described in the literature [34,35]. Carbon nanotubes were synthesized by catalytic decomposition of acetylene over transition metal catalyst supported on the MMT surfaces in order to modify the polymer matrix with these nanoadditives. The purpose of the work was to verify catalytic potential of montmorillonite used as a modifier of coal tar pitches subjected to thermal conversion to a carbon phase. At room temperature pitch is a solid, consisting of a complex mixture of numerous predominantly aromatic and heterocyclic hydrocarbons [36]. We have assumed that during coal tar pitch pyrolysis at elevated temperature gaseous hydrocarbon compounds are evolved, including PAH, which, in the presence of the ceramic nanofiller, can be decomposed with the formation of a carbon phase [23]. We expected that the catalytic decomposition process would lead to reduce the evolution of harmful gaseous products.

Two types of CTPs that differ in their physical and chemical properties have been used to investigate the effects of MMT addition on the structure and resulting properties of carbon samples obtained at 1000 °C and 2000 °C. Both pitches differed significantly in the amount of polycyclic aromatic hydrocarbons evolving during heat treatment.

2. Materials and methods

2.1. Materials

Two types of commercially available pitches (CTP—soft coal tar pitch and HCTP—hard coal tar pitch) that differed in Mettler softening point (SP), Alcan coking value (CV), and PAH content were used in the study. The soft coal tar pitch was provided by Deza a.s. (Czech Republic), and the hard coal tar pitch, commercially available under the name Carbores P, was provided by Rutgers Basic Aromatics, (Germany).

Characteristic parameters of the pitches are listed in Table 1. Both pitches were modified with nano MMT K-10 clay (CAS no. 1318-93-0) provided by Sigma Aldrich with a surface area of 250 m^2/g.

2.2. Sample preparation

Prior to the preparation of samples, the ceramic powder was dispersed in ethanol suspension by sonication, for 15 min. Each sample consisted of 5 g of powder and 20 mL of ethanol. Pitches were ground and sieved to the fraction 0.4–0.6 mm. Subsequently, the sonicated

Table 1
Characteristics of coal tar pitches.

Properties	CTP	HCTP
Density [g/cm^3]	1.27	1.35
Softening point–Mettler [°C]	103.3	234.5
Coking value- Alcan [%]	54.0	83.0
PAH content [mg/g]	183.9	3.6

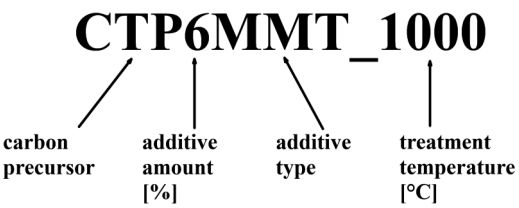

Fig. 1. Denotation of samples.

suspension of MMT in ethanol was mixed with soft and hard pitch powders at ambient temperature for 5 min, and the mixtures were put into a dryer at 70 °C for 24 h. After ethanol evaporation, preliminary homogenized mixtures of the pitches with montmorillonite were obtained. Next, MMT-containing pitches were melted and additionally stirred in liquid state. The homogenization temperatures for the soft and hard pitches were 165 °C and 295 °C, respectively. Optimum homogenization parameters of nanoparticles in the pitches were established in our previous work [16]. The suspensions of pitches containing different contents of montmorillonite (0–10 wt%) were prepared.

Before the carbonization process the CTP/ceramic nanoparticles composites were not subjected to the pretreatment oxidation. In this work, we investigated the effect of ceramic nanoparticles on the properties of CTPs as binders for carbon and graphite materials. Such binders do not require pretreatment in an oxidizing atmosphere before carbonization.

After the homogenization, the samples were annealed at 1000 °C and 2000 °C, at a heating rate of 10 °C/min, under an argon flow of 90 L/h. The following denotation for the samples was used in the work (Fig. 1).

2.3. Methods

A Cole-Parmer 130P ultrasonic processor with a ¼" microtip for nanoparticle de-agglomeration was used with 60% amplitude. A power of 10.5 W was applied for the preparation of MMT in ethanol suspension. SEM micrographs of the samples were carried out using a Nova Nano SEM 200 microscope connected with an Energy Dispersive Spectroscopy (EDS) EDAX point analyzer. A Jeol JSM 5400 SEM microscope connected with a LINK ISIS 300 EDS instrument from Oxford Instruments was used for mapping EDS. The mass changes (TG) and differential scanning calorimetry analysis (DSC) of the samples were made with the simultaneous thermal analysis (STA) using 449 F3 NETZSCH SDT system. The DSC and TG studies were performed at a heating rate of 10 °C/min under a nitrogen atmosphere using the samples of about 5 mg in weight. For TEM investigations, a Titan 80–300 high-resolution electron microscope (S/TEM) from FEI Company was used.

For X-ray diffraction (XRD) analyzes, an X'Pert Pro from Philips was used. The measurements were made using a copper radiation source lamp (CuKα1, $\lambda = 0.154056$ nm). The samples were prepared in a powder form. The microstructural parameters *i.e.*, the crystallite thickness L_c, as well as the interplanar distance between the graphene planes d_{002} were determined from the diffraction patterns. Using the Scherrer formula, $L_c = k\lambda/(B\cos\theta)$, and the Bragg formula, $n\lambda = 2d\sin\theta$, parameters L_c corresponding to the apparent crystallites sizes in the [002] direction of the graphite structure and d_{002} were determined. λ is the wavelength of the X-rays, B is the half width at peak maximum (rad), θ is the Bragg angle (in rad) and k is the Scherrer constant taken as 1.

Raman spectroscopy measurements were made using a Horiba LabRAM HR spectrometer with a camera using a laser with an excitation wavelength of 532 nm. The measurements were performed in the range from 4000 to 0 cm^{-1}. The spectrum was obtained from averaging three micro-areas of the material. To evaluate the crystallinity of the