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Carbon nanotubes synthetized from gaseous products of waste polymer pyrolysis and their application

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ABSTRACT

This work is dedicated to the synthesis of carbon nanotube from pyrolysis gases obtained by plastics. Virgin and waste plastics (polyethylene, polypropylene, polystyrene, polyamide, polyvinyl-chloride, municipal plastic waste) were used as raw materials and fed into a horizontal tubular reactor and pyrolyzed without catalyst at 560–570 °C. Raw materials could be transformed into 14–32% gases and 15–44% pyrolysis oils, depending on the type of raw materials. Pyrolysis of municipal plastic waste produced the highest gas yield, while pyrolysis of virgin polypropylene gave the highest oil yield. Gases were passed through a chemical vapour deposition reactor, where they were transformed into carbon nanotubes at 700 °C in a semi-continuous rotating reactor with 0.5 h reaction time. To enhance the transformation of pyrolysis gases into carbon nanotubes (CNTs), Fe and Co based catalysts were used. Both gaseous and oil products of pyrolysis were investigated by gas-chromatography. The produced CNTs were added as reinforcement into a commercial low density polyethylene matrix using heated two roll mill and then specimens for testing were manufactured. Especially the reinforcing effects of carbon nanotube were investigated through the measuring of tensile and Charpy impact properties of the CNTs-LDPE polymers.

1. Introduction

Carbon nanotubes (CNTs) with different structure have a great interest in engineering. Different forms of CNTs are commercially available. They are allotropes of carbon, and were discovered in the beginning of 1990s' CNTs have excellent mechanical, thermal and electrical properties and very low mass/volume ratio; they have up to 100 GPa tensile strength and even over 1000 GPa E-modulus [1]. Thefore, CNTs are idea materials to be applied in the fields, where the low density, low weight and high tensile strength or elastic moduli are required (e.g. transportation, structural materials, high-tech application, etc.). The structure of CNT is like a rolled-up graphene sheet, where the diameter is in the range of nanometre. Depending on the rolling-up, single-wall nanotube and multi-wall nanotube could be classified. It is also well known, that owing to the electron structure in CNTs, their electrical properties change as a function of temperature.

CNT synthesis could be occurred from different sources: hydrocarbons in gaseous and liquid form or even waste polymers, providing an alternative method for waste management. A. Bazargan and G. McKay summarized the different methods for CNT synthesis from plastic wastes. It was suggested that chemical vapour deposition (CVD), catalytic chemical vapour deposition (CCVD), arc discharge, high pressure carbon-monoxide disproportion, laser ablation, are preferential technologies for CNT production, regarding the reactor constructions, autoclave, quartz tube, muffle furnace or fluidized bed [2–5]. Both the CNT production and the properties of CNTs were significantly affected by the reactor construction and raw materials. One of the crucial points of the synthesis is the catalyst poisoning by the pollutants inside the raw materials, such as chlorine, which could dramatically deteriorate the formation of CNT.

CNT production also has disadvantages e.g. the high operation temperature and high energy consuming [1,6]. Regarding process parameters, the required cost and high temperature could be

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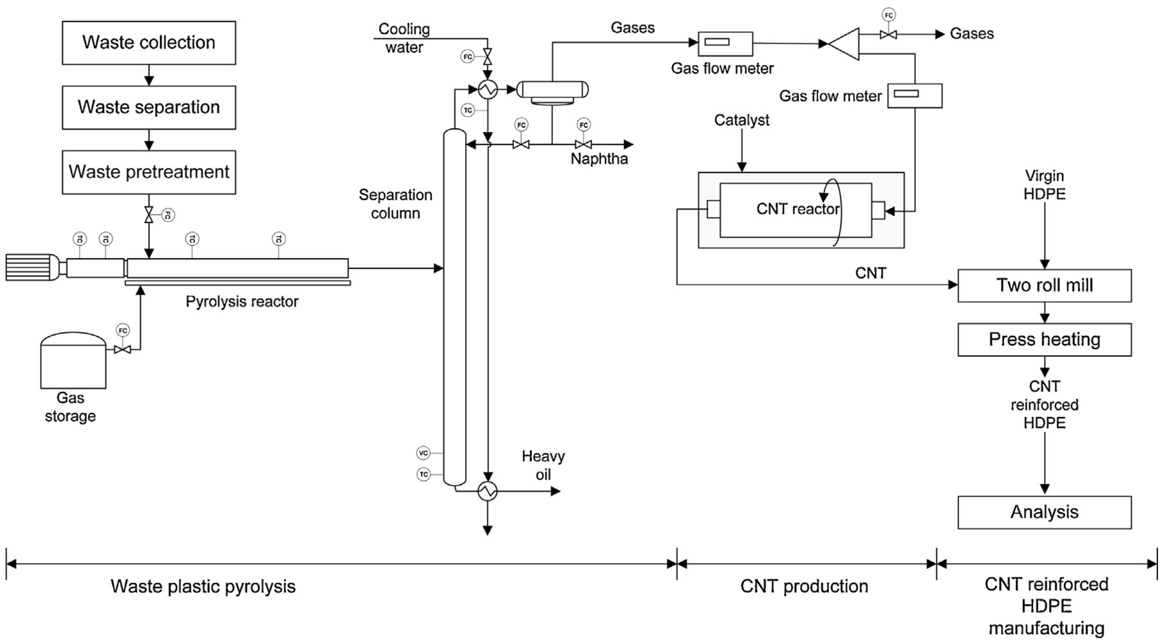

Fig. 1. Layout of the process.

decreased by developing efficient catalysts or by optimizing the reactor construction. For example, a comparative low temperature (450–480 °C) process was used with a fluidized bed was reported for catalytic CNT production from polyolefins [5].

Recently CNTs were synthetized from waste polymers using catalysts such as Ni [7,8], Ni/Zn, Ni/Ca, Ni/Mg, Ni/Ce, Ni/Al [9–12] or Ni/Mo/Mg [4,13]. In general the metal particles are impregnated in the surface of catalyst support (e.g. Al_2O_3) and the interaction between them is essential for the growth of CNTs. More amounts of metals impregnated on the support surface decrease the inner diameter of CNT [13], as well as the ratio of different metals is also a crucial parameter. It was also found that the filamentous carbon production was higher using polyethylene, than polypropylene or polystyrene [12].

Not only waste plastics (polyethylene, polypropylene, polystyrene, polyethylene-terephthalate) and hydrocarbon gases, but also pyrolysis oils could be also used for CNT production. High phenolic containing pyrolysis oil was obtained from printed circuit board, and then hollow-centred and straight CNT was prepared through pyrolysis oil based resin in experimental work of Quan et al. [14]. It is important to remark that beside CNT, the production of hydrogen is also advantageous during waste plastic CNT transformation. For example, Nahil et al. [15] investigated several Ni-based catalyst for the coproduction of CNTs and hydrogen from pyrolysis of waste plastics followed by in-line catalytic reforming of pyrolysis vapours, using a two stage reaction system (first stage pyrolysis at 500 °C and second stage catalytic reforming at 800 °C). They reported that the addition of Mn into Ni-Al catalyst significantly enhanced the production of carbon nanotubes, compared to other metals such as Ca, Ce and Zn, while the hydrogen yield with Ni-Mn-Al catalyst was also relative high. It was suggested that the weak interaction between metal particles and catalyst support was important for the growth of CNTs. Similar process has been used to converting real waste plastics into hydrogen and CNTs [16]. The authors reported that the presence of Cl (0.3 wt.% polyvinyl chloride in waste HDPE) showed clear negative effect on the formation of CNTs, while the presence of sulphur has shown less influence on CNTs production in terms of quality and CNT morphologies. In addition, the influences of process parameters such as carbon/steam ration, catalyst amount and reaction temperature on the coproduction of CNTs and hydrogen from catalytic thermo-chemical conversion of waste plastics were reported [9,12,17]. The CNT quality, purity and morphology could be also affected by the addition of steam [1]. In some cases CNT was synthetized by catalyst free approaches; e.g. waste PET mineral water bottles were crashed and pyrolyzed to produce nano channelled ultrafine CNT, multi walled CNT and nano-sized solid carbon spheres by arc discharge technique at temperatures up to 2600 °C [18].

It is well known that waste polymers occur serious environmental problem. The chemical recycling of plastic and biomass wastes should be one of the options for their long term sustainable utilization. During chemical recycling the long carbon chain polymers are transferrable into gases and fuel oils, however the further application of pyrolysis products are still opened question. Owing to the structure of products, generally their possibility for energetic applications is investigated. It was well demonstrated, that the pyrolysis of polyethylene and polypropylene could generate such products, which have favourable hydrocarbon composition and low contaminants. Contaminants in pyrolysis products are an important parameter, because their high level is responsible for limited re-application. Refineries and petrochemical plants have strict limitations against their raw materials and products in the European Union, therefore pyrolysis oils with high level of contaminants are difficult to be utilized e.g. blending to fuel.

In this work waste plastics were pyrolyzed in a horizontal tubular reactor producing hydrocarbon gases at 560–570 °C without catalysts. Then resulted gases were driven into a catalytic chemical vapour deposition (CCVD) reactor, where CNT was produced in the presence of Fe or Co based catalyst. The synthetized CNTs were further applied as reinforcement in low density polyethylene matrix.

2. Experimental

2.1. Waste plastics for pyrolysis

Real plastic waste and commercial virgin polymers have been used for CNT production as raw materials. Their main properties are summarized in Table 1, in which considerable differences