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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 0.5h 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.

Keywords: waste plastics; pyrolysis, carbon nanotube; gases; catalyst; application

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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 100GPa tensile strength and even over 1000GPa 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 [2,3,4,5]. 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 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 [9,10,11,12] 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 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 was demonstrated both on the chemical structure and also in contaminants of raw materials. Five of the eight plastics were commercial virgin polymers: high-density polyethylene (HDPE, supplied by MOL Petrolkémia Plc), polypropylene (PP, supplied by MOL Petrolkémia Plc), polystyrene (PS, supplied by Versalis Spa), polyamide 6 (PA, supplied by BASF AG) and polyvinyl-chloride (PVC, Supplied by BorsodChem Co). Polyamide had 12.4% nitrogen and 12.7% oxygen, while polyvinyl-chloride had 32.6% chlorine content, beside carbon and hydrogen. Owing to waste source of the remain raw materials (waste HDPE, waste PP and waste MPW), they had contaminants, such as Cl, N, S, Ca, Zn and P in the range of 177 mg kg^{-1} and 3108 mg kg^{-1}. Regarding the contaminants in waste HDPE, the calcium (1464 mgkg^{-1}) had the highest concentration, while the zinc content (1832 mgkg^{-1}) was the highest in case of the waste PP.

From Table 1, the MPW contained 4.04% lube oils and 1.08% absorbed water on the waste particles surfaces, indicating that the contaminant level was considerable higher; in the range of 991 mg kg^{-1} and 3108 mg kg^{-1}. Plastic particles of the MPW were analyzed and identified by Fourier-transformed Infrared Spectroscopy, including high-density polyethylene (93.1%), polypropylene (4.9%), poly-vinyl chloride (0.2%), label and paper (1.8%). Regarding the commercial virgin polymers, negligible ash content was obtained (< 0.001%), while higher level of inorganic compounds was found in case of the waste sourced raw materials (1.25-3.41%). Due to the functional group in structure of polyamide, it had the highest moisture content (2.79%). To investigate the ability of the plastics for CNT production the following 8 samples were used: 100% virgin HDPE, 100% virgin PP, 80% virgin HDPE+20%virgin PS, 99% virgin HDPE+1% virgin PVC, 99% virgin HDPE+1% virgin PA, 50% waste HDPE+50% waste PP, 100% waste HDPE and 100% MPW (see Table 2).

2.2. Process for CNT production from waste plastics

CNT was synthetized from the gas fractions of waste polymer pyrolysis, according to the process demonstrated in Figure 1. Raw materials had been pyrolyzed in an electrically heated tubular reactor at 560-570°C without catalysts using same feed rate (0.5kg h^{-1}). The reason of pyrolysis temperature was twofold. In one hand owing to the reactor construction it was a limitation regarding the application of high temperature (e.g. formation of coke deposition on reactor inside wall). On the other hand it was not preferred to increase the undesired compounds in pyrolysis oil formed at high temperature. In the case of real waste raw materials, they had been shredded and milled into suitable particle size (2-4mm); then they were feed through an electrically heated extruder, where the polymers melted between 205-280°C. The extruder was directly connected to the tubular pyrolysis reactor. The tubular reactor has a special screw inside to reduce coke deposition on reactor wall and avoid its fouling. Inside the reactor the long carbon chain of raw materials was cracked into vapours of gases and liquids. The reactor temperature was measured and controlled by thermocouples and PID controllers in four different points along the reactor length, respectively. Pyrolysis products were separated into gases, pyrolysis oil and heavy oil in an atmospheric distillation column with L/D ratio of 15. The separation column consists of packed bed and water cooled multi-tubular heat exchanger. The cooling water was driven in shell side. The top temperature was between 140 and 150°C, while the bottom temperature was 370-380°C. Product yields were calculated using the following equation:

$$\text{Yield (\%)} = \frac{m_i}{\sum_{i=1}^{3} m_i} \cdot 100 \qquad \text{(Eq. 1)}$$

Where m_i is the weight of products (1=gases, 2=light oil, 3=heavy oil). Both gases and pyrolysis oil were analyzed by gas-chromatography to determine more about their composition.

Following the pyrolysis section the gas products were driven into a CCVD reactor, which was a semi-continuous rotating reactor. In CCVD reactor pyrolysis gases has been transformed into CNT at 700°C using 0.5 h reaction time. CNT was reported to be produced from the pyrolysis gases using Fe and Co containing catalysts (cobalt-acetate and iron-acetate were impregnated in 2.5-2.5 w/w % on silica-alumina) in a semi-continuous rotating reactor [19,20]. After the reaction, the CNT product was taken out by a vacuum equipment into a sample-holder.

2.3. Manufacturing of CNT reinforced LDPE composites

Plastic derived CNTs were tested as reinforcements in commercial virgin low-density polyethylene (LDPE (BRALEN NA 7-25) supplied by MOL Petrolkémia Plc). The reinforcement was mixed into matrix by a laboratory two roll mill machine (Lab Tech LRM-S-110/T3E, Labtech Ltd, Thailand) using 180°C and 210°C roll temperatures. CNT reinforced LDPE was ground by a laboratory grinder (Dipre type) into particles below 5mm, then 1mm x 100mm x 100mm composite sheets was manufactured by a CARVER type hydraulic hot press using 180°C and 5,000 psi pressure. Following the hot press procedure 1mm x 10mm x 100mm specimens were cut from the sheets for further testing.

2.4. Analytical methods

DANI gas-chromatograph was used for gas and pyrolysis oil analyses. For gas analysis 50 m x 0.32 mm fused silica column with Al_2O_3/KCl coating was used under isothermal conditions, while a 30 m x 0.32 mm Rtx-11 (Crossbond1, 100% dimethyl polysiloxane) column was used for pyrolysis oils analysis with a flame ionization detector. Regarding the pyrolysis oil, the following the temperature program was used: at 30°C for 5min, using 15°C/min from 30°C to 350°C and at 350°C for 10 min. Components were analysed according to their retention time, using chromatography library. In case of pyrolysis oil, they were dissolved in n-pentane.

Results of gas-chromatography was completed with results of Fourier transformed infrared spectroscopy (FTIR). For determination of main chemical groups of compounds a TENSOR 27 type Fourier transformed infrared spectrometer was used (resolution: 2 cm^{-1}, illumination: SiC Globar light, monocromator: Littrow prism, detector: RT-DLaTGS (Deutero L-α-Alanine Triglycin-Sulphate) type detector with KBr window) in the 400-4000cm^{-1} wave number range.

The morphologies of CNTs were examined using a scanning electron microscopy (SEM) (Cambridge instruments (Stereoscan 360)). In addition, transmission electron microscopy of CNTs was obtained using JEOL 2010 equipment.

To determine the tensile properties, an INSTRON 3345 universal tensile testing machine was used according to MSZ EN ISO 527-1-4:1999. The temperature in the laboratory was 20°C and the relative humidity was 60% during the mechanical tests. Tensile tests were carried out at 20 mm min^{-1} crosshead speed. Five independent samples had been tested in each case, and then the mean value was calculated. CEAST Resil Impactor was applied to measure Charpy impact strength of the produced samples according to MSZ EN ISO 179-2:2000 standard.

3. Results and discussions

3.1. Plastic pyrolysis for gas production

3.1.1. Product yields

Figure 2 summarizes the product yield obtained by pyrolysis at 560-570°C. It is known that the energetic application is the main utilization of the pyrolysis products, especially pyrolysis oil. According to our earlier work mild cracking conditions was preferable for production of gases, pyrolysis oil and heavy oil without aromatic formation or even coke deposition on the reactor internal wall [21,22]. Figure 2 demonstrates considerable differences on the yields of different products. The gas yield was in a range of 14.6% (virgin HDPE) and 32.6% (MPW), while the pyrolysis oil changed between 15.8% (virgin HDPE) and 32.5% (MPW). The higher volatile product yields of samples containing PP and PS can be explained with the difference in activation energy of the polymers. For example, PP and PS has lower activation energy than HDPE, because the thermal stability of tertiary carbon atom is lower for the PP and PS samples. Therefore polypropylene or polystyrene could be degraded easier than polyethylene at the same circumstance and results in higher yields of liquids and gases. Regarding polystyrene and polyethylene, significantly higher yields of pyrolysis oil was found using fluidized bed at 550°C, or even in case of pyrolysis-reforming at 500 and 700°C, respectively [23,24]. However, significantly a lower yield of oil was found by laboratory screw kiln reactor in case of mixed polymer waste [25].

Comparing the results from virgin plastic pyrolysis and waste plastic pyrolysis, it could be concluded that pyrolysis of waste plastics produced higher gas and pyrolysis oil yields than the pyrolysis of virgin plastics. For example, pyrolysis of the virgin HDPE produced 14.7% gases and 15.8% pyrolysis oil, while 22.2% of gas yield and 29.4% of oil yield were obtained in the case of using the waste HDPE. It is suggested that presumably contaminants could initiate the decomposition reactions of polymer main chain, promoting the intensive C-C cracking. Similar phenomenon was found regarding the PVC and PA. Either pyrolysis gas and oil yields were higher, when 1% PVC or 1% PA was added into HDPE. Earlier results demonstrated that instable radicals or molecule fragments could be obtained from the pyrolysis of PVC and PA, which could promote the degradation of polyethylene [26,27].

3.1.2. Gas composition

The composition of gas products are summarized in Table 2. It is indicated that pyrolysis of the 100% virgin HDPE, 99% HDPE+1%PVC, 99%HDPE+1%PA, 100% waste HDPE and MPW produced significant C_2, C_3 and C_4 compounds, while gases obtained from pyrolysis of PP contained high amounts of C_3 hydrocarbons (propene and propane). Adding 20% PS to the commercial virgin HDPE, the C_2 and C_4 hydrocarbon proportion was the highest.

The branching structure of polypropylene resulted high concentrations of branched hydrocarbons in gaseous products. 11.5% i-butane and 6.0% i-pentene was measured in gases using the virgin PP, while the concentrations of i-butane and i-pentene were 8.0% and 5.72, respectively, in the case of 50% waste HDPE+50% waste PP. Gases containing nearly half of olefins was suggested to be due to the β-scission reactions. It is also clear that the hydrocarbon composition of gaseous fraction changed slightly by the addition of 1% PA or PVC. However considerable contaminants could be measured in samples. Based on laboratory screw kiln pyrolysis of mixed polymer waste, M. Day et al demonstrated that the yield of propylene had maximum at 600°C, while that of ethylene increased as function of pyrolysis temperature [25]. However, the hydrogen was the main component in case of HDPE pyrolysis in spouted bed-fixed bed pyrolysis-steam reforming [24].

It is also clear that the source of raw materials such as virgin or waste plastic considerably affected the contaminant quantity in the gas product. For example, gases obtained from the pyrolysis of50%-50% waste HDPE and waste PP had 1055 mg kg^{-1} Cl, 316 mg kg^{-1} N, 115 mg kg^{-1} S and 158 mg kg^{-1} P. However the pyrolysis of virgin HDPE, PP and PS resulted gases without contaminants. The highest concentrations of Cl, N, S and P in gas product were obtained from MPW pyrolysis: 2410 mgkg^{-1}, 1937 mgkg^{-1}, 1073 mgkg^{-1}, 934 mgkg^{-1}, respectively. The average calculated heating value of gases was around 46MJ kg^{-1}, which is high enough to provide the heat requirement of the pyrolysis process. However, pyrolysis gases containing contaminants such as Cl and S are difficult to be utilized to provide energy due to the limitations of gas engine.

3.1.3. Composition of pyrolysis oil and heavy oil

Figure 3 demonstrates the pyrolysis oils composition measured by gas-chromatography and FTIR method. Pyrolysis oil had aliphatic non-branched and branched, aromatic and naphtehic hydrocarbons. It is known that aliphatic (especially branched) and moderately aromatics are the mostly favoured compounds for further energetic utilization. The thermal decomposition of polyethylene and polypropylene produced aliphatic hydrocarbons, because the 560°C temperature was quite low for aromatization reactions. It has been reported that aromatization reactions of aliphatic compounds were taken over 600°C during the waste/virgin polymer pyrolysis using tubular reactor and fluidized bed reactor [21,28,29]. On the other hand, 22.6% aromatics, especially styrene and ethyl-benzene, were obtained in the pyrolysis oil obtained from the pyrolysis of 80% virgin HDPE+20% virgin PS. Brominated polystyrene pyrolysis resulted vast amount of styrene and ethyl-benzene in fluidized bed reactor [23], however also significant yield of aromatics was found in case of mixed plastic waste pyrolysis in laboratory screw kiln reactor, which was increased by the temperature [25]. In that case 5.4% naphtenes was also involved in the oil. It is important to remark that the pyrolyis of waste sourced polyethylene and polypropylene also produced aromatic compounds: 3.1%, 3.8% and 4.1% in the case of 50% waste HDPE+50% waste PP, waste HDPE and MPW pyrolysis, respectively. Presumably, contaminants could be functioned as precursors for the cracking of C-C bonds or the aromatization of aliphatic compounds. It is noted that high concentration of branched aliphatic compounds could be found using polypropylene raw materials. It was due to that polypropylene structure contains tertiary carbon atoms in the main polymer frame. 64.7% and 48.2% concentrations of branched aliphatic compounds were measured in the pyrolysis oil produced from the pyrolysis of virgin PP and 50% waste HDPE+50% waste PP, respectively. Comparing results with pyrolysis oil composition e.g. in tandem spouted bed-fixed bed reactor it was concluded, that mainly isoparaffins and olefins in C_5-C_{11} carbon range were involved in pyrolysis oils obtained from HDPE pyrolysis-steam reforming [24].

Furthermore, higher branched hydrocarbon content was obtained using waste sourced plastics, compared to virgin polymers, or even the presence of PVC and PA also increased the production of branched molecule compounds. For example, branched aliphatic concentration was 10.2% in the case of virgin HDPE, which was increased to 16.3% (99% virgin HDPE+1% virgin PVC) and 14.9% (99% virgin HDPE+1% virgin PA). Both polyamide and poly-vinyl-chloride are decomposed through consecutive reaction steps mechanism. The first reaction step produces instable molecule fragments having lower activation energies than the decompositions of polyethylene. Presumably those instable molecule fragments could be involved in the formation of branched structured compounds e.g. by radical initiated intramolecular or intermolecular hydrogen transfer reactions (R-CH_3-CH_3-CH_2* (R-CH_3-CH_2*-CH_3 or R-CH_3-CH_3-CH_2*+ R-CH_3-CH_3-R (R-CH_3-CH_3-CH_3 + R-CH_3-CH_2*-R), which result in the isomerisation of main frame and increasing the concentration of the branched aliphatic compounds. Table 3 summarizes some of the main properties of pyrolysis oils and heavy oils. The pyrolysis oils have densities between 0.801g/cm^3 and 0.810g/cm^3 at 20°C, depending on the raw materials. Each of them has yellow colour and their boiling point ranges were 24-293°C. The colour of heavy oils changed from yellow to light grey. They have solid appearance in room temperature, because the melting point was 59-62°C, however the initial boiling point was 245-252°C.

3.2. Nanotube production from gases

According to gas compositions, the theoretical carbon content of gases was between 85.6% (virgin HDPE pyrolysis) and 86.9% (virgin PP pyrolysis), indicating that theoretically 85.6-86.9% of gaseous products could be transformed into CNTs. Figure 4 summarizes the theoretical amounts of CNT production using gases produced from pyrolysis of different plastics (g CNT/100g raw material unit) and the conversions. The conversion was calculated as following (Eq. 1):

$$C = \frac{m_{CNT}}{m_{CNT}\,(\text{theoretical})} \cdot 100 \qquad \text{(Eq. 2)}$$

Where "m_{CNT}" is the amount of CNT synthetized in experiment and "m_{CNT} (theoretical)" is the theoretical amount of CNT production. Based on product yields, the theoretical value of CNT production was also calculated using Eq. 2, which was between 12.54 and 27.9 g (CNT g^{-1} raw material).

$$TCNTP = \frac{A \cdot Y_{gases}}{100} \qquad \text{(Eq. 3)}$$

Where "TCNTP" is the theoretical CNT production in g CNT $100g^{-1}$ raw material unit, "A" is the theoretical carbon content of gases and "Y_{gases}" is the yield of gases in pyrolysis.

Due to the high gas yields of using virgin PP, MPW and 50% waste HDPE+50% waste PP pyrolysis, these raw material resulted in high values of theoretical CNT production with 24.7, 27.9 and 23.0 (g CNT 100 g^{-1} raw material), respectively.

Figure 4 also summarizes the conversion (Eq. 1), which was in a broad range between 35.9% and 65.9%. It is noted that the theoretical carbon content was in a relative narrow range (85.6-86.9%). The conversion of CNT production was 35.6% using virgin HDPE, while it was 54.0% or 43.3% using virgin PP or 80% virgin HDPE+20% virgin PS raw material, respectively. In general, higher conversion could be achieved using real waste raw materials: 48.1% (50% waste HDPE+50% waste PP), 47.1% (waste HDPE) and 60.7% (MPW). It is an important observation, that polyamide in raw material also supported the higher conversion of CNT production (65.9%); however, the presence of PVC in raw material showed disadvantageous, because the conversion was only 36.5%. It is indicated that due to the addition of 1% polyamide, the CNT conversion increased by 83.7% (HDPE/PA mixture) compared to virgin HDPE.

Figure 4 also shows the amount of CNT produced from 100 g raw material. Due to high gas yields in the case of using virgin PP, 50% waste HDPE+50% waste PP and MPW pyrolysis, the amount of produced CNT was also high (13%, 11% and 17% related to the raw material, respectively). On the other hand, because of the high conversion, experiments using 99% virgin HDPE+1% virgin PA has also generated high amount of CNT (11% of the raw material). Presumably the oxygen content of the polyamide promoted the activity for CNT production.

Figure 5 shows the SEM results of the synthetized CNTs produced from the 8 samples. Bundles of fibres could be observed for all the CNTs samples. Although the size of these bundles (with diameter up to 10 nm) is not uniform and it is difficult to obtain clear differences between these CNTs samples, the further examination using SEM and TEM indicates that these bundles consists of hundreds of uniform filamentous carbons (Figure 6 (a)). A SEM picture with lower magnification (Figure 6 (a)) shows that the length of the carbon bundle could be up to 50 µm. TEM analysis (Figure 5(b)) indicates these filamentous carbons are mostly CNTs. In addition, the diameter of each individual CNT seems to be around 20 nm, as shown from the TEM results (Figure 5 (b)). High resolution images of TEM (Figure 6 (b)) also show that many defects are presented in the CNTs, in terms of the construction of carbon nano-sheets (chirality and number of walls). Therefore, it is suggested CNTs with uniform diameters were successfully obtained using all the plastic samples.

3.3. Application of nanotubes for plastic reinforcing

In order to investigate the reinforcing effect of the synthetized nanotubes, they were blended into commercial LDPE using a two-roll mill (mass ratio of CNTs and LDPE is: 0.5%). Figure 7 demonstrates the tensile strength and E-moduli of specimens. The virgin LDPE has tensile strength and E-modulus of 16.5MPa and 642MPa, respectively. From Figure 7, considerably higher tensile strength and modulus could be measured for the CNT-LDPE composites, compared to the virgin LDPE. The tensile strength changed between 16.9 and 23.5MPa. It is clear that CNT containing composites related to 99% virgin HDPE+1% virgin PVC and MPW raw materials showed the lowest tensile strength; 16.9MPa and 17.7MPa, respectively. Both of the two raw materials had high chlorine content. Presumably chlorine could disadvantageously affect the surface morphology of CNT, therefore weak interfacial forces could be obtained between the CNT and LDPE in the CNT-LDPE composite. For virgin HDPE and 80% virgin HDPE+20% virgin PS, significant differences between the tensile strength and tensile modulus can be found from figure 7, which could be explained by the presence of polystyrene in raw material. Aromatic side chain in polystyrene structure could be modifying the surface of CNT to obtain better interfacial connection between CNT and LDPE matrix.

It is important to remark that the tensile strength was significantly higher in relation to the raw materials with other contamination. It is important to remark, that contaminants or other atoms besides carbon and hydrogen in raw materials have disadvantageous to the further energetic application of pyrolysis products. Those elements decrease the storage stability of pyrolysis products or even can cause problem during transportation. That is why the advantageous properties of polyamide or even contaminants during the CNT production is very desired phenomena. For example, the tensile strength was 21.5MPa using 99% virgin HDPE+1% virgin PA raw material, indicating a 30.3% increase compared to the virgin LDPE. The highest tensile strength (23.5MPa) with 42.4% increasing was measured, when the CNT was obtained from the gases produced from the pyrolysis of 80% virgin HDPE+20% virgin PS pyrolysis. Regarding tensile modulus, similar trends with tensile strength could be observed. The presence of chlorine inside the raw plastic materials had a clear disadvantageous effect to the tensile elongation of CNT-LDPE composite; for example, 693MPa (MPW) and 745MPa (99% virgin HDPE+1% virgin

PVC) were the two lowest values. On the contrary, significant increasing in tensile modulus was found when the CNT was obtained from CCVD process using the gases produced from the pyrolysis of 80% virgin HDPE+20% virgin PS (1009MPa, 57.2% increasing) or 50% waste HDPE+50% waste PP (911MPa, 41.9% increasing). The specimen density and the Charpy impact strength are summarized in Figure 8. One of the most advantageous properties of the CNT reinforced polymer composites is the decreasing in density, or lower weight/volume ratio, which could be lead a lower fuel consumption for vehicles using CNT reinforced composites. The matrix LDPE had density of 0.919g cm^{-3}, which could be decreased to 0.861-881g cm^{-3}. It is demonstrated that 4.1-6.3% weight decreasing of given volume unit CNT-LDPE composite could be reached. Regarding Charpy impact strength, in the case of 80% virgin HDPE+20% virgin PS raw material, the lowest value (13.9kJ m^{-2}, with only 3.7% increasing), however this CNT-LDPE composite had showed the most advanced tensile properties. Commercial virgin LDPE had 13.4kJ m^{-2} impact strength.

4. Conclusion

In this work carbon nanotube was synthetized from gaseous products produced from pyrolysis of waste plastics, and then the CNTs were tested for reinforcing LPDE. Gaseous products of pyrolysis contained hydrocarbons bellow C_6, which were also contaminated with Cl, S or N in the case using real waste polymers. It was found that the presence of polyamide in the raw material had an advantageous effect to the conversion of CNT production, however, the presence of PVC had disadvantages. Based on SEM and TEM analyses, the synthetized CNTs had lots of similarities in their morphology. Regarding the testing of CNTs in LDPE matrix, one of the most advantageous properties of the CNT reinforced polymer composites is the decreasing in density, as well as the tensile or even the Charpy impact strengths could be also significantly increased.

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Reference

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Figures and Tables

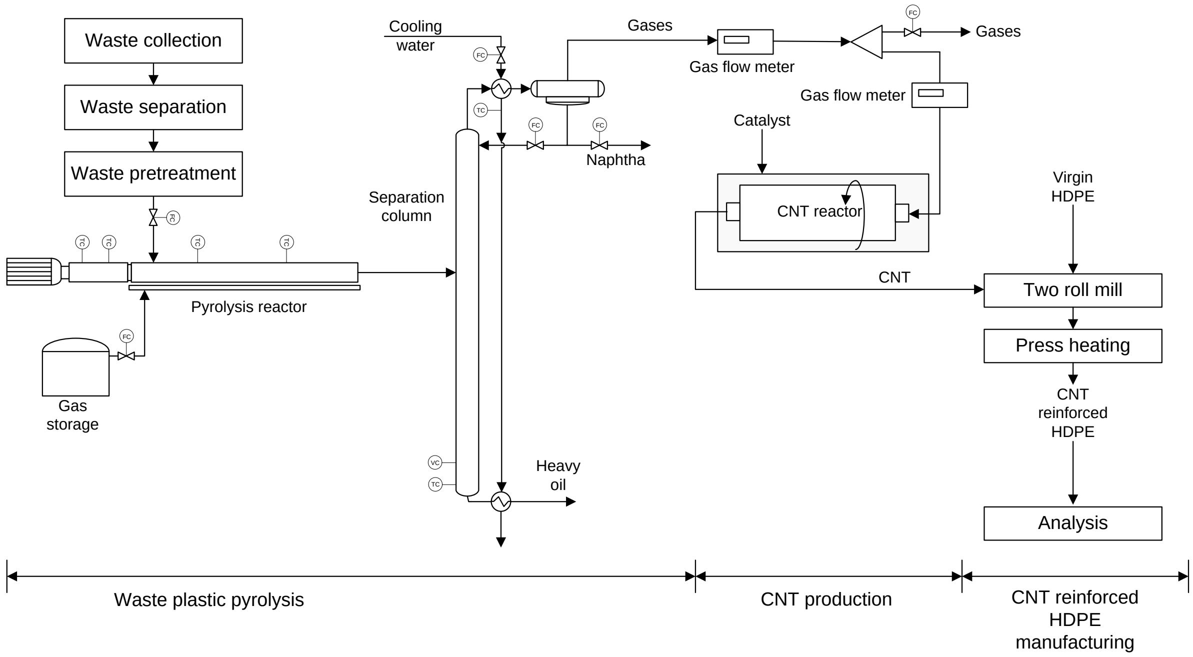


Figure 1
Layout of the process

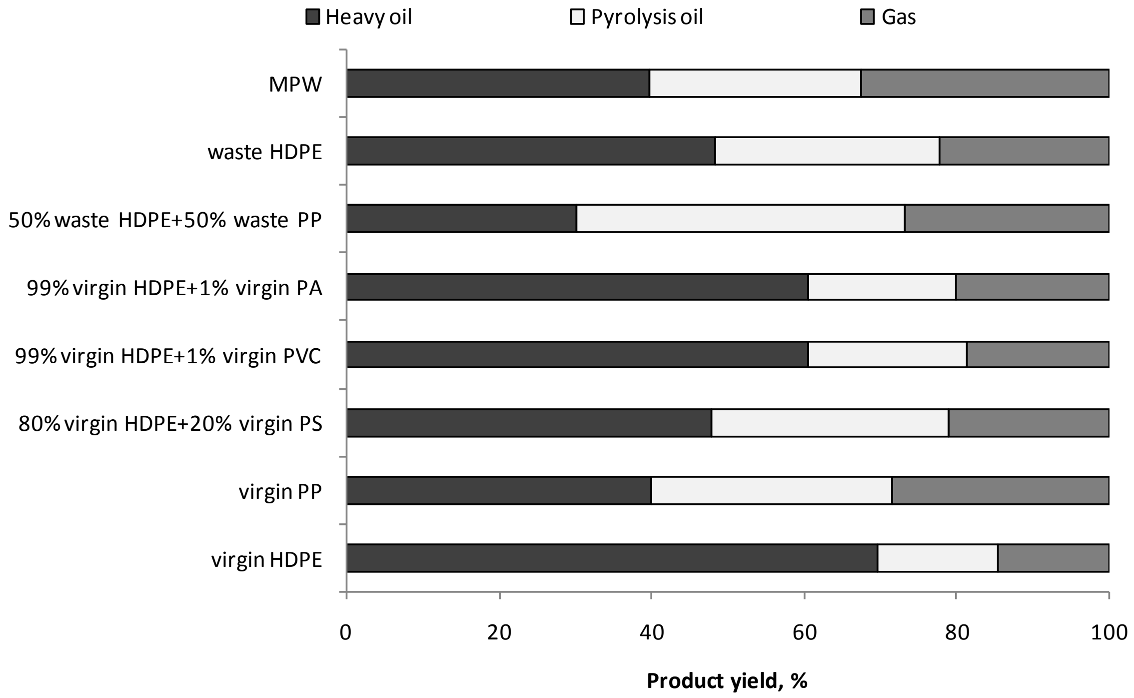


Figure 2

Product yields obtained from plastic pyrolysis

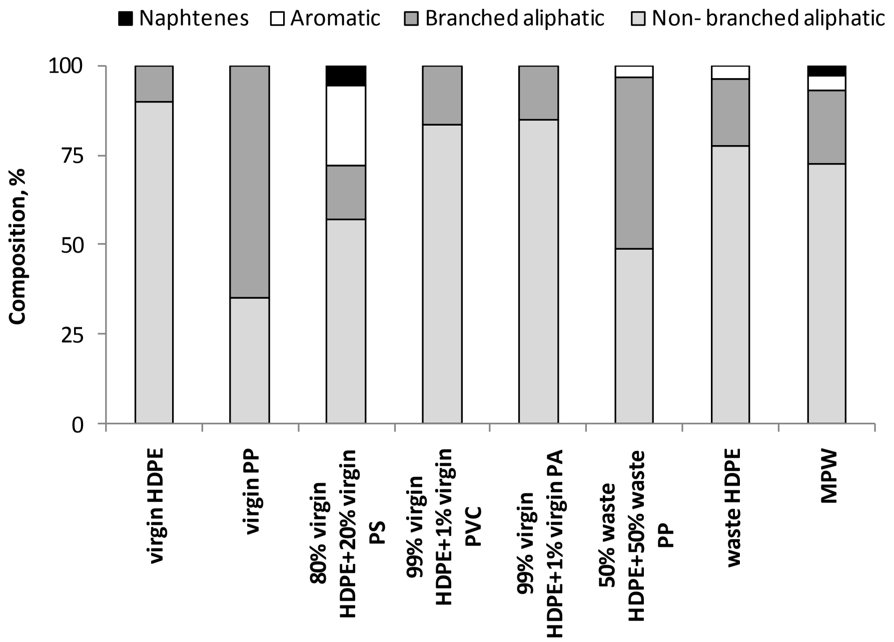


Figure 3
Composition of pyrolysis oils

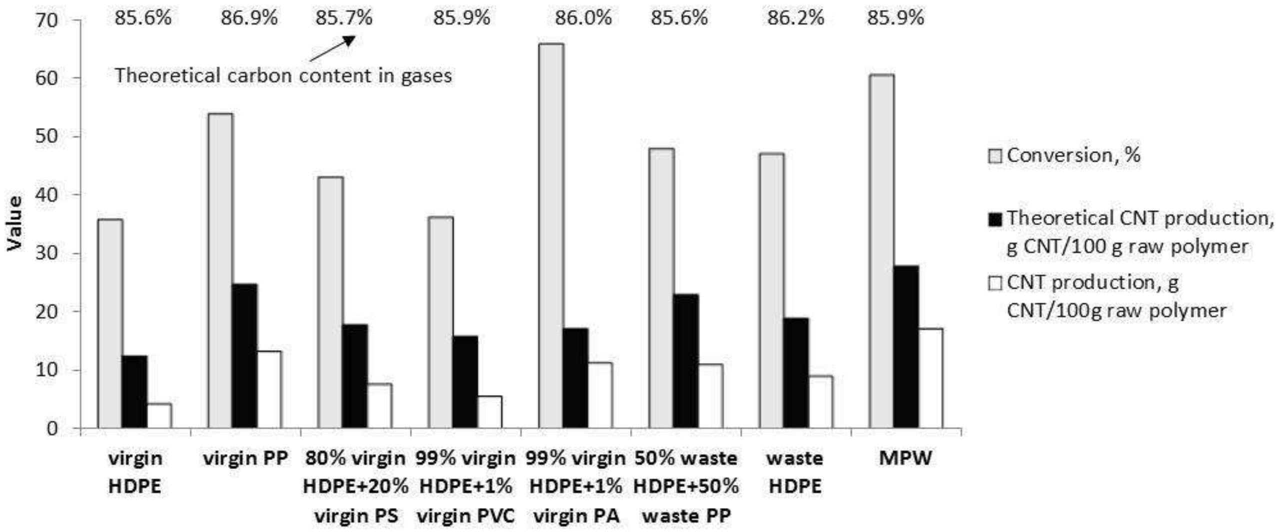


Figure 4

CNT production from gases

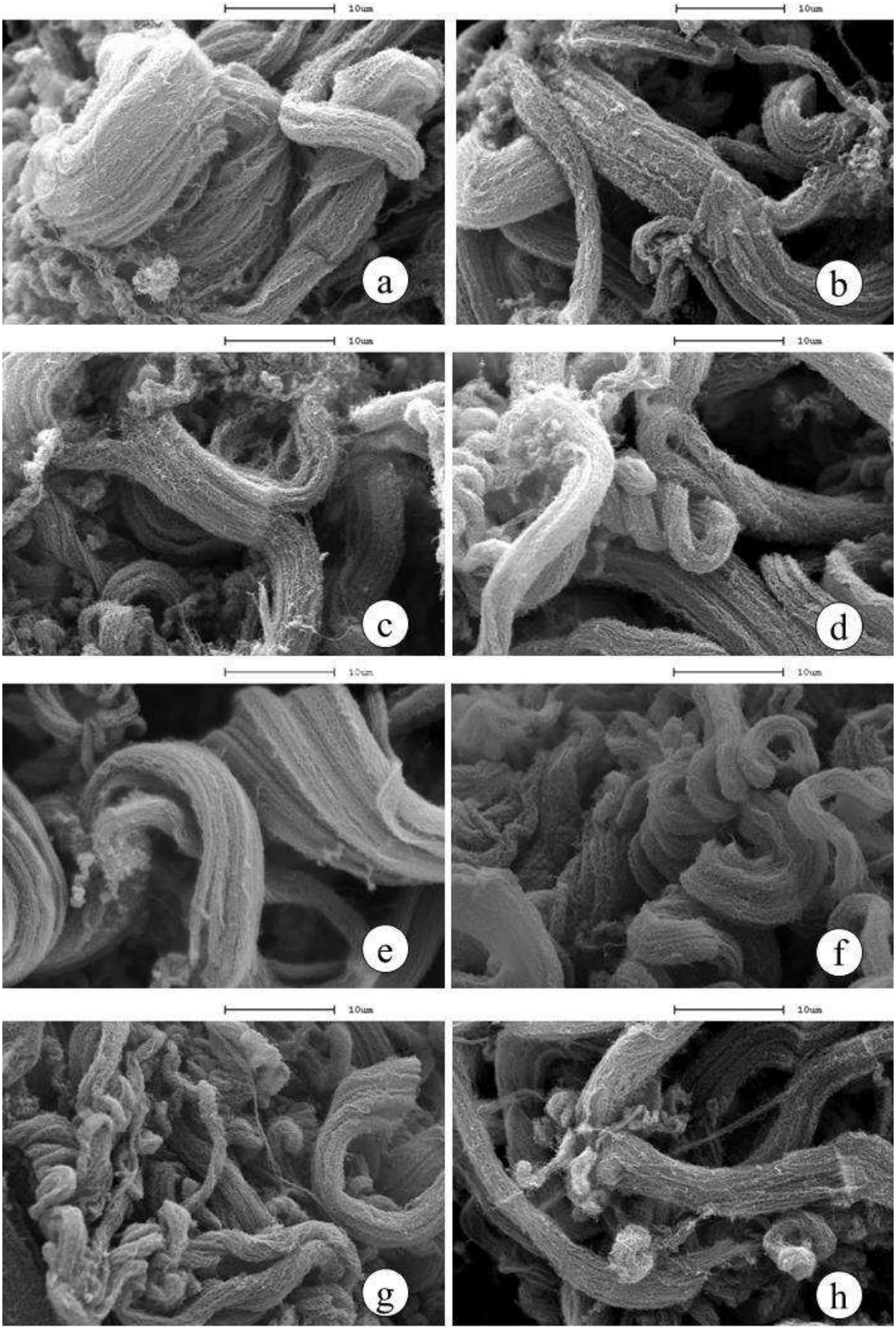
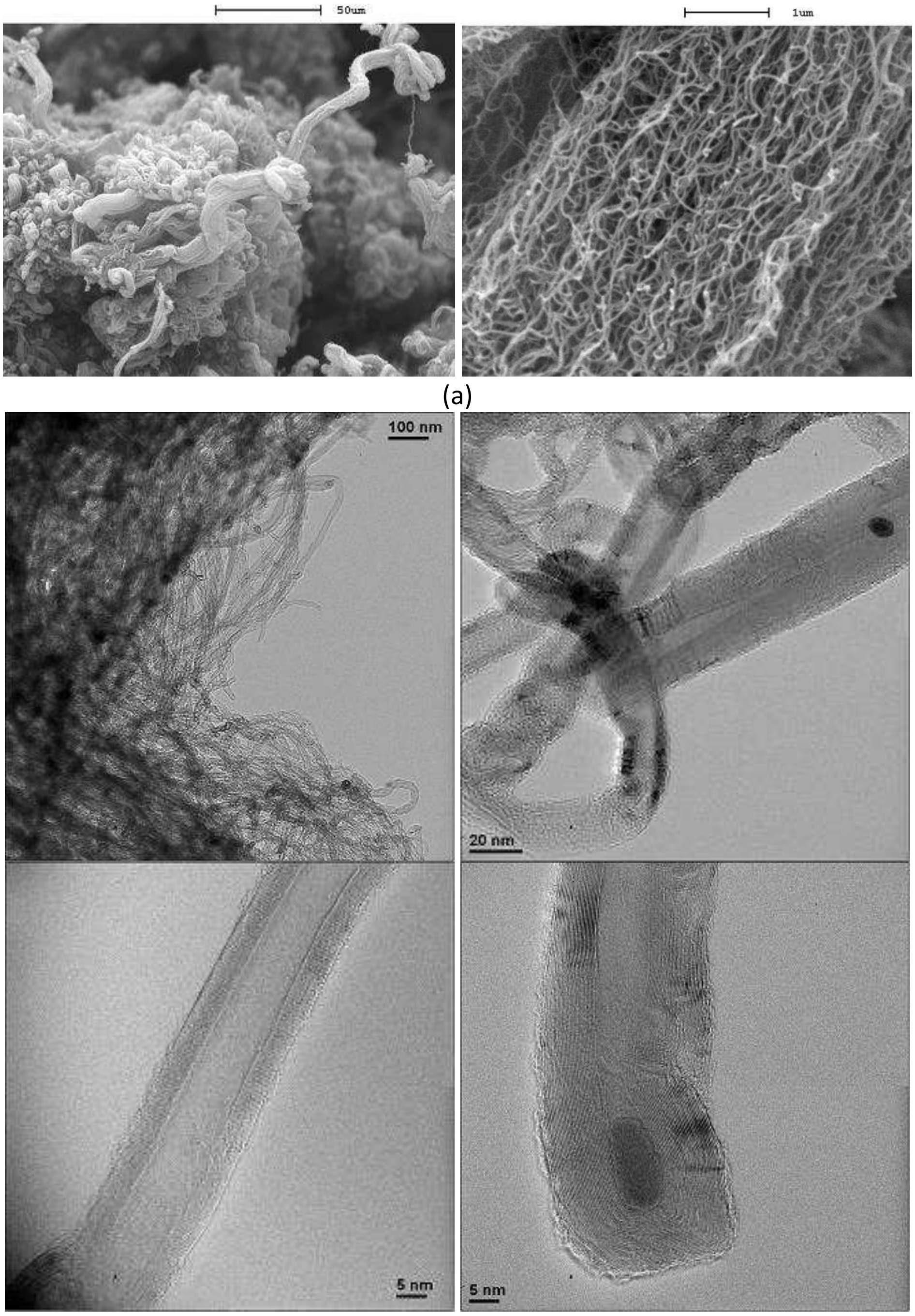


Figure 5
SEM micrographs of synthetized CNT
((a)-virgin PP, (b)-virgin HDPE, (c)- 80% virgin HDPE+20% virgin PS, (d)-99% virgin HDPE+1%virgin PVC, (e)-99% virgin HDPE+1%virgin PA, (f)- 50% waste HDPE+50% waste PP, (g)-waste HDPE, (h)-MPW)



(a)

(b)

Figure 6

Typical SEM (a) and TEM (b) micrographs of synthetized CNT

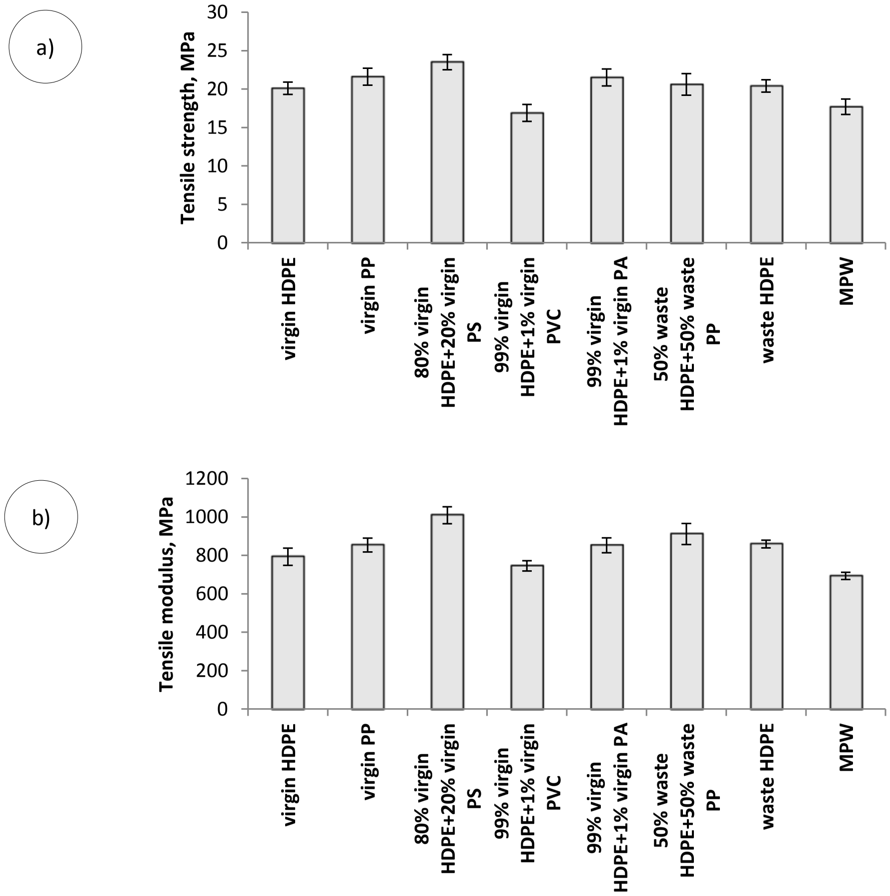


Figure 7

Tensile strength (a) and E-modulus (b) of CNT reinforced LDPE composites

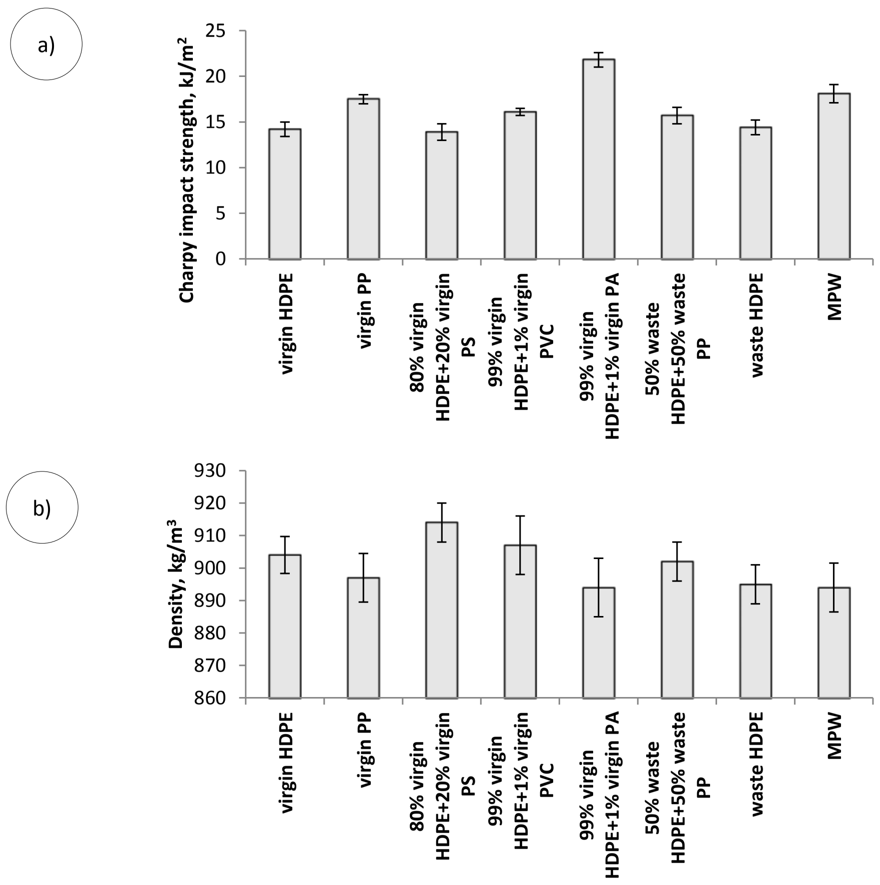


Figure 8

Charpy impact strength (a) and densities (b) of CNT reinforced LDPE composites

Table 1
Main properties of polymers

	HDPE	PP	PS	PA	PVC	w HDPE	w PP	w MPW
Origin	virgin	virgin	virgin	virgin	virgin	waste	waste	waste
Ash content, %	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	1.25	2.41	3.41
Carbon	85.2 %	84.8 %	92.1 %	66.4 %	59.2 %	85.1 %	85.4 %	85.9%
Hydrogen	14.8 %	15.2 %	7.9 %	8.5 %	8.2 %	14.9 %	14.6 %	14.1%
Oxygen	-	-	-	12.7 %	-	-	-	-
Chlorine	-	-	-	-	32.6 %	522 mg kg^{-1}	-	2730 mg kg^{-1}
Nitrogen	-	-	-	12.4 %	-	470 mg kg^{-1}	177 mg kg^{-1}	2062 mg kg^{-1}
Sulphur	-	-	-	-	-	215 mg kg^{-1}	273 mg kg^{-1}	991 mg kg^{-1}
Calcium	-	-	-	-	-	1464 mg kg^{-1}	1106 mg kg^{-1}	1490 mg kg^{-1}
Zinc	-	-	-	-	-	882 mg kg^{-1}	1819 mg kg^{-1}	1832 mg kg^{-1}
Phosphorous	-	-	-	-	-	341 mg kg^{-1}	-	3108 mg kg^{-1}
Oil contamination, %	-	-	-	-	-	-	-	4.04
Moisture, %	0.72	0.44	0.71	2.79	0.55	1.10	1.28	1.08

Table 2

The composition of gases obtained by plastic waste pyrolysis and their contaminants

	Compounds	**virgin HDPE**	**virgin PP**	**80% virgin HDPE+20% virgin PS**	**99% virgin HDPE+1% virgin PVC**	**99% virgin HDPE+1% virgin PA**	**50% waste HDPE+50% waste PP**	**waste HDPE**	**MPW**
Hydrocarbons	Methane	5.8	4.8	10.3	5.0	7.9	5.7	4.2	6.4
	Ethene	17.3	8.0	12.3	13.8	14.6	11.6	15.6	16.6
	Ethane	8.6	4.2	7.4	9.5	9.6	9.7	10.6	9.7
	Propene	10.3	28.6	11.9	16.2	16.9	12.2	18.8	14.4
	Propane	12.7	24.8	10.2	11.9	11.5	10.7	13.5	9.6
	Butene	13.8	3.9	17.0	17.4	18.9	15.4	11.7	15.6
	Butane	9.4	3.1	12.2	12.7	11.3	13.2	11.0	13.8
	i-butane	3.8	11.5	3.5	3.1	2.9	8.0	4.5	4.5
	Pentene	7.5	2.5	5.6	4.9	1.7	3.6	2.4	2.4
	Pentane	6.6	2.0	6.4	2.7	2.1	3.0	2.5	3.2
	i-pentene	2.9	6.0	2.1	0.5	0.7	5.2	1.6	2.5
	Hexene	1.1	0.4	1.1	1.8	1.5	1.4	1.9	0.9
	Hexane	0.2	0.2	0.3	0.5	0.4	0.2	1.7	0.4
Conta- minants	Chlorine	-	-	-	1131 mg kg^{-1}	-	1055 mg kg^{-1}	-	2410 mg kg^{-1}
	Nitrogen	-	-	-	-	833 mg kg^{-1}	316mg kg^{-1}	149 mg kg^{-1}	1937 mg kg^{-1}
	Sulphur	-	-	-	-	-	115 mg kg^{-1}	725 mg kg^{-1}	1073 mg kg^{-1}
	Phosphorous	-	-	-	-	-	158mg kg^{-1}	-	934 mg kg^{-1}

Table 3
Pyrolysis oil and heavy oil properties

	Raw material	virgin HDPE	virgin PP	80% virgin HDPE+20% virgin PS	99% virgin HDPE+1% virgin PVC	99% virgin HDPE+1% virgin PA	50% waste HDPE+50% waste PP	waste HDPE	MPW
Pyrolysis	**Colour**	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow
	Density, g/cm^3	0.810	0.801	0.806	0.804	0.810	0.809	0.808	0.804
	Boiling point, °C	25-289	25-290	24-292	25-284	28-293	24-285	25-289	24-290
Heavy oil	**Colour**	yellow	yellow	yellow	light brown	light grey	light yellow	light grey	light grey
	Melting point, °C	62	59	60	61	64	61	60	60
	Flash point, °C	214	209	210	209	211	211	210	209
	Viscosity at 80°C, mm^2/s	4.7	4.4	4.5	4.6	4.7	4.6	4.7	4.7
	Boiling point, °C	247-	245-	250-	249-	252-	248-	249-	250-