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34 1. Introduction

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

44 CNT synthesis could be occurred from different sources: hydrocarbons in gaseous and liquid form or even
45 waste polymers, providing an alternative method for waste management. A. Bazargan and G. McKay summarized
46 the different methods for CNT synthesis from plastic wastes. It was suggested that chemical vapour deposition
47 (CVD), catalytic chemical vapour deposition (CCVD), arc discharge, high pressure carbon-monoxide
48 disproportion, laser ablation, are preferential technologies for CNT production, regarding the reactor constructions,
49 autoclave, quartz tube, muffle furnace or fluidized bed [2,3,4,5]. Both the CNT production and the properties of
50 CNTs were significantly affected by the reactor construction and raw materials. One of the crucial points of the
51 synthesis is the catalyst poisoning by the pollutants inside the raw materials, such as chlorine, which could
52 dramatically deteriorate the formation of CNT.

53 CNT production also has disadvantages e.g. the high operation temperature and high energy consuming [1,6].
54 Regarding process parameters, the required cost and high temperature could be decreased by developing efficient
55 catalysts or by optimizing the reactor construction. For example, a comparative low temperature (450-480°C)
56 process was used with a fluidized bed was reported for catalytic CNT production from polyolefins [5].

57 Recently CNTs were synthesized from waste polymers using catalysts such as Ni [7,8], Ni/Zn, Ni/Ca, Ni/Mg,
58 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
59 catalyst support (e.g. Al₂O₃) and the interaction between them is essential for the growth of CNTs. More amounts
60 of metals impregnated on the support surface decrease the inner diameter of CNT [13], as well as the ratio of
61 different metals is also a crucial parameter. It was also found that the filamentous carbon production was higher
62 using polyethylene, than polypropylene or polystyrene [12].

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

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

93 In this work waste plastics were pyrolyzed in a horizontal tubular reactor producing hydrocarbon gases at
94 560-570°C without catalysts. Then resulted gases were driven into a catalytic chemical vapour deposition (CCVD)
95 reactor, where CNT was produced in the presence of Fe or Co based catalyst. The synthesized CNTs were further
96 applied as reinforcement in low density polyethylene matrix.

97

98 **2. Experimental**

99 **2.1. Waste plastics for pyrolysis**

100 Real plastic waste and commercial virgin polymers have been used for CNT production as raw materials.
101 Their main properties are summarized in Table 1, in which considerable differences was demonstrated both on the
102 chemical structure and also in contaminants of raw materials. Five of the eight plastics were commercial virgin
103 polymers: high-density polyethylene (HDPE, supplied by MOL Petrolkémia Plc), polypropylene (PP, supplied by
104 MOL Petrolkémia Plc), polystyrene (PS, supplied by Versalis Spa), polyamide 6 (PA, supplied by BASF AG) and
105 polyvinyl-chloride (PVC, Supplied by BorsodChem Co). Polyamide had 12.4% nitrogen and 12.7% oxygen, while
106 polyvinyl-chloride had 32.6% chlorine content, beside carbon and hydrogen. Owing to waste source of the remain
107 raw materials (waste HDPE, waste PP and waste MPW), they had contaminants, such as Cl, N, S, Ca, Zn and P in
108 the range of 177 mg kg⁻¹ and 3108 mg kg⁻¹. Regarding the contaminants in waste HDPE, the calcium (1464 mgkg⁻¹)
109 had the highest concentration, while the zinc content (1832 mgkg⁻¹) was the highest in case of the waste PP.

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

120

121 **2.2. Process for CNT production from waste plastics**

122 CNT was synthesized from the gas fractions of waste polymer pyrolysis, according to the process
123 demonstrated in Figure 1. Raw materials had been pyrolyzed in an electrically heated tubular reactor at 560-570°C

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

$$138 \quad \text{Yield (\%)} = \frac{m_i}{\sum_{i=1}^3 m_i} \cdot 100 \quad (\text{Eq. 1})$$

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

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

147

148 2.3. Manufacturing of CNT reinforced LDPE composites

149 Plastic derived CNTs were tested as reinforcements in commercial virgin low-density polyethylene (LDPE
150 (BRALEN NA 7-25) supplied by MOL Petrolkémia Plc). The reinforcement was mixed into matrix by a laboratory
151 two roll mill machine (Lab Tech LRM-S-110/T3E, Labtech Ltd, Thailand) using 180°C and 210°C roll
152 temperatures. CNT reinforced LDPE was ground by a laboratory grinder (Dipre type) into particles below 5mm,

153 then 1mm x 100mm x 100mm composite sheets was manufactured by a CARVER type hydraulic hot press using
154 180°C and 5,000 psi pressure. Following the hot press procedure 1mm x 10mm x 100mm specimens were cut from
155 the sheets for further testing.

156

157 **2.4. Analytical methods**

158 DANI gas-chromatograph was used for gas and pyrolysis oil analyses. For gas analysis 50 m x 0.32 mm
159 fused silica column with Al₂O₃/KCl coating was used under isothermal conditions, while a 30 m x 0.32 mm Rtx-
160 11 (Crossbond1, 100% dimethyl polysiloxane) column was used for pyrolysis oils analysis with a flame ionization
161 detector. Regarding the pyrolysis oil, the following the temperature program was used: at 30°C for 5min, using
162 15°C/min from 30°C to 350°C and at 350°C for 10 min. Components were analysed according to their retention
163 time, using chromatography library. In case of pyrolysis oil, they were dissolved in n-pentane.

164 Results of gas-chromatography was completed with results of Fourier transformed infrared spectroscopy
165 (FTIR). For determination of main chemical groups of compounds a TENSOR 27 type Fourier transformed
166 infrared spectrometer was used (resolution: 2 cm⁻¹, illumination: SiC Global light, monochromator: Littrow prism,
167 detector: RT-DLaTGS (Deutero L- α -Alanine Triglycin-Sulphate) type detector with KBr window) in the 400-
168 4000cm⁻¹ wave number range.

169 The morphologies of CNTs were examined using a scanning electron microscopy (SEM) (Cambridge
170 instruments (Stereoscan 360)). In addition, transmission electron microscopy of CNTs was obtained using JEOL
171 2010 equipment.

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

177

178 **3. Results and discussions**

179 **3.1. Plastic pyrolysis for gas production**

180 **3.1.1. Product yields**

181 Figure 2 summarizes the product yield obtained by pyrolysis at 560-570°C. It is known that the energetic
182 application is the main utilization of the pyrolysis products, especially pyrolysis oil. According to our earlier work
183 mild cracking conditions was preferable for production of gases, pyrolysis oil and heavy oil without aromatic

184 formation or even coke deposition on the reactor internal wall [21,22]. Figure 2 demonstrates considerable
185 differences on the yields of different products. The gas yield was in a range of 14.6% (virgin HDPE) and 32.6%
186 (MPW), while the pyrolysis oil changed between 15.8% (virgin HDPE) and 32.5% (MPW). The higher volatile
187 product yields of samples containing PP and PS can be explained with the difference in activation energy of the
188 polymers. For example, PP and PS has lower activation energy than HDPE, because the thermal stability of tertiary
189 carbon atom is lower for the PP and PS samples. Therefore polypropylene or polystyrene could be degraded easier
190 than polyethylene at the same circumstance and results in higher yields of liquids and gases. **Regarding polystyrene
191 and polyethylene, significantly higher yields of pyrolysis oil was found using fluidized bed at 550°C, or even in
192 case of pyrolysis-reforming at 500 and 700°C, respectively [23,24]. However, significantly a lower yield of oil
193 was found by laboratory screw kiln reactor in case of mixed polymer waste [25].**

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

203

204 3.1.2. Gas composition

205 The composition of gas products are summarized in Table 2. It is indicated that pyrolysis of the 100% virgin
206 HDPE, 99% HDPE+1%PVC, 99%HDPE+1%PA, 100% waste HDPE and MPW produced significant C₂, C₃ and
207 C₄ compounds, while gases obtained from pyrolysis of PP contained high amounts of C₃ hydrocarbons (propene
208 and propane). Adding 20% PS to the commercial virgin HDPE, the C₂ and C₄ hydrocarbon proportion was the
209 highest.

210 The branching structure of polypropylene resulted high concentrations of branched hydrocarbons in gaseous
211 products. 11.5% i-butane and 6.0% i-pentene was measured in gases using the virgin PP, while the concentrations
212 of i-butane and i-pentene were 8.0% and 5.72, respectively, in the case of 50% waste HDPE+50% waste PP. Gases
213 containing nearly half of olefins was suggested to be due to the β -scission reactions. It is also clear that the

214 hydrocarbon composition of gaseous fraction changed slightly by the addition of 1% PA or PVC. However
215 considerable contaminants could be measured in samples. Based on laboratory screw kiln pyrolysis of mixed
216 polymer waste, M. Day et al demonstrated that the yield of propylene had maximum at 600°C, while that of
217 ethylene increased as function of pyrolysis temperature [25]. However, the hydrogen was the main component in
218 case of HDPE pyrolysis in spouted bed-fixed bed pyrolysis-steam reforming [24].

219 It is also clear that the source of raw materials such as virgin or waste plastic considerably affected the
220 contaminant quantity in the gas product. For example, gases obtained from the pyrolysis of 50%-50% waste HDPE
221 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
222 virgin HDPE, PP and PS resulted gases without contaminants. The highest concentrations of Cl, N, S and P in gas
223 product were obtained from MPW pyrolysis: 2410 mgkg⁻¹, 1937 mgkg⁻¹, 1073 mgkg⁻¹, 934 mgkg⁻¹, respectively.
224 The average calculated heating value of gases was around 46MJ kg⁻¹, which is high enough to provide the heat
225 requirement of the pyrolysis process. However, pyrolysis gases containing contaminants such as Cl and S are
226 difficult to be utilized to provide energy due to the limitations of gas engine.

227

228 **3.1.3. Composition of pyrolysis oil and heavy oil**

229 Figure 3 demonstrates the pyrolysis oils composition measured by gas-chromatography and FTIR method.
230 Pyrolysis oil had aliphatic non-branched and branched, aromatic and naphthelic hydrocarbons. It is known that
231 aliphatic (especially branched) and moderately aromatics are the mostly favoured compounds for further energetic
232 utilization. The thermal decomposition of polyethylene and polypropylene produced aliphatic hydrocarbons,
233 because the 560°C temperature was quite low for aromatization reactions. It has been reported that aromatization
234 reactions of aliphatic compounds were taken over 600°C during the waste/virgin polymer pyrolysis using tubular
235 reactor and fluidized bed reactor [21,28,29]. On the other hand, 22.6% aromatics, especially styrene and ethyl-
236 benzene, were obtained in the pyrolysis oil obtained from the pyrolysis of 80% virgin HDPE+20% virgin PS.
237 Brominated polystyrene pyrolysis resulted vast amount of styrene and ethyl-benzene in fluidized bed reactor [23],
238 however also significant yield of aromatics was found in case of mixed plastic waste pyrolysis in laboratory screw
239 kiln reactor, which was increased by the temperature [25]. In that case 5.4% naphthenes was also involved in the
240 oil. It is important to remark that the pyrolysis of waste sourced polyethylene and polypropylene also produced
241 aromatic compounds: 3.1%, 3.8% and 4.1% in the case of 50% waste HDPE+50% waste PP, waste HDPE and
242 MPW pyrolysis, respectively. Presumably, contaminants could be functioned as precursors for the cracking of C-
243 C bonds or the aromatization of aliphatic compounds. It is noted that high concentration of branched aliphatic

244 compounds could be found using polypropylene raw materials. It was due to that polypropylene structure contains
245 tertiary carbon atoms in the main polymer frame. 64.7% and 48.2% concentrations of branched aliphatic
246 compounds were measured in the pyrolysis oil produced from the pyrolysis of virgin PP and 50% waste
247 HDPE+50% waste PP, respectively. Comparing results with pyrolysis oil composition e.g. in tandem spouted bed-
248 fixed bed reactor it was concluded, that mainly isoparaffins and olefins in C₅-C₁₁ carbon range were involved in
249 pyrolysis oils obtained from HDPE pyrolysis-steam reforming [24].

250 Furthermore, higher branched hydrocarbon content was obtained using waste sourced plastics, compared to
251 virgin polymers, or even the presence of PVC and PA also increased the production of branched molecule
252 compounds. For example, branched aliphatic concentration was 10.2% in the case of virgin HDPE, which was
253 increased to 16.3% (99% virgin HDPE+1% virgin PVC) and 14.9% (99% virgin HDPE+1% virgin PA). Both
254 polyamide and poly-vinyl-chloride are decomposed through consecutive reaction steps mechanism. The first
255 reaction step produces instable molecule fragments having lower activation energies than the decompositions of
256 polyethylene. Presumably those instable molecule fragments could be involved in the formation of branched
257 structured compounds e.g. by radical initiated intramolecular or intermolecular hydrogen transfer reactions (R-
258 CH₃-CH₃-CH₂* (R-CH₃-CH₂*-CH₃ or R-CH₃-CH₃-CH₂*+ R-CH₃-CH₃-R (R-CH₃-CH₃-CH₃ + R-CH₃-CH₂*-R),
259 which result in the isomerisation of main frame and increasing the concentration of the branched aliphatic
260 compounds. Table 3 summarizes some of the main properties of pyrolysis oils and heavy oils. The pyrolysis oils
261 have densities between 0.801g/cm³ and 0.810g/cm³ at 20°C, depending on the raw materials. Each of them has
262 yellow colour and their boiling point ranges were 24-293°C. The colour of heavy oils changed from yellow to light
263 grey. They have solid appearance in room temperature, because the melting point was 59-62°C, however the initial
264 boiling point was 245-252°C.

265

266 3.2. Nanotube production from gases

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

$$272 \quad C = \frac{m_{\text{CNT}}}{m_{\text{CNT}}(\text{theoretical})} \cdot 100 \quad (\text{Eq. 2})$$

273 Where “ m_{CNT} ” is the amount of CNT synthesized in experiment and “ m_{CNT} (theoretical)” is the theoretical
274 amount of CNT production. Based on product yields, the theoretical value of CNT production was also calculated
275 using Eq. 2, which was between 12.54 and 27.9 g (CNT g⁻¹ raw material).

$$276 \quad TCNTP = \frac{A \cdot Y_{gases}}{100} \quad (Eq. 3)$$

277 Where “TCNTP” is the theoretical CNT production in g CNT 100g⁻¹ raw material unit, “A” is the theoretical
278 carbon content of gases and “ Y_{gases} ” is the yield of gases in pyrolysis.

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

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

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

296 Figure 5 shows the SEM results of the synthesized CNTs produced from the 8 samples. Bundles of fibres
297 could be observed for all the CNTs samples. Although the size of these bundles (with diameter up to 10 nm) is not
298 uniform and it is difficult to obtain clear differences between these CNTs samples, the further examination using
299 SEM and TEM indicates that these bundles consists of hundreds of uniform filamentous carbons (Figure 6 (a)). A
300 SEM picture with lower magnification (Figure 6 (a)) shows that the length of the carbon bundle could be up to 50
301 μ m. TEM analysis (Figure 5(b)) indicates these filamentous carbons are mostly CNTs. In addition, the diameter

302 of each individual CNT seems to be around 20 nm, as shown from the TEM results (Figure 5 (b)). High resolution
303 images of TEM (Figure 6 (b)) also show that many defects are presented in the CNTs, in terms of the construction
304 of carbon nano-sheets (chirality and number of walls). Therefore, it is suggested CNTs with uniform diameters
305 were successfully obtained using all the plastic samples.

306

307 **3.3. Application of nanotubes for plastic reinforcing**

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

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

332 PVC) were the two lowest values. On the contrary, significant increasing in tensile modulus was found when the
333 CNT was obtained from CCVD process using the gases produced from the pyrolysis of 80% virgin HDPE+20%
334 virgin PS (1009MPa, 57.2% increasing) or 50% waste HDPE+50% waste PP (911MPa, 41.9% increasing). The
335 specimen density and the Charpy impact strength are summarized in Figure 8. One of the most advantageous
336 properties of the CNT reinforced polymer composites is the decreasing in density, or lower weight/volume ratio,
337 which could be lead a lower fuel consumption for vehicles using CNT reinforced composites. The matrix LDPE
338 had density of 0.919g cm^{-3} , which could be decreased to $0.861\text{-}0.881\text{g cm}^{-3}$. It is demonstrated that 4.1-6.3% weight
339 decreasing of given volume unit CNT-LDPE composite could be reached. Regarding Charpy impact strength, in
340 the case of 80% virgin HDPE+20% virgin PS raw material, the lowest value (13.9kJ m^{-2} , with only 3.7%
341 increasing), however this CNT-LDPE composite had showed the most advanced tensile properties. Commercial
342 virgin LDPE had 13.4kJ m^{-2} impact strength.

343

344 **4. Conclusion**

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

353

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357 **Reference**

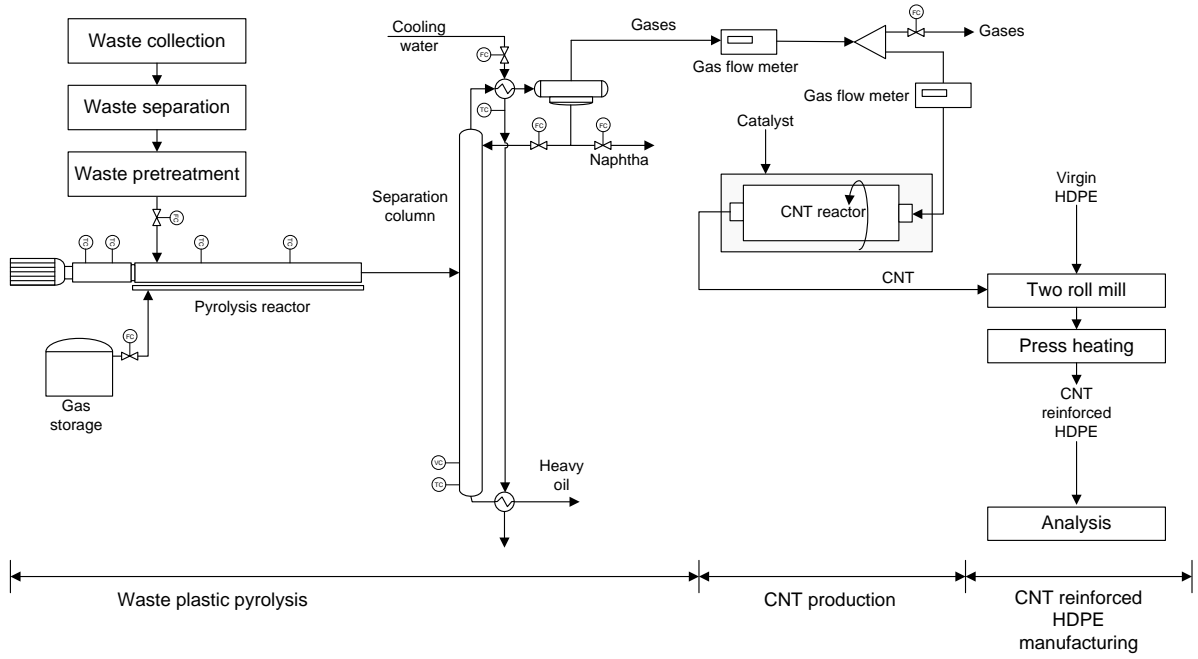
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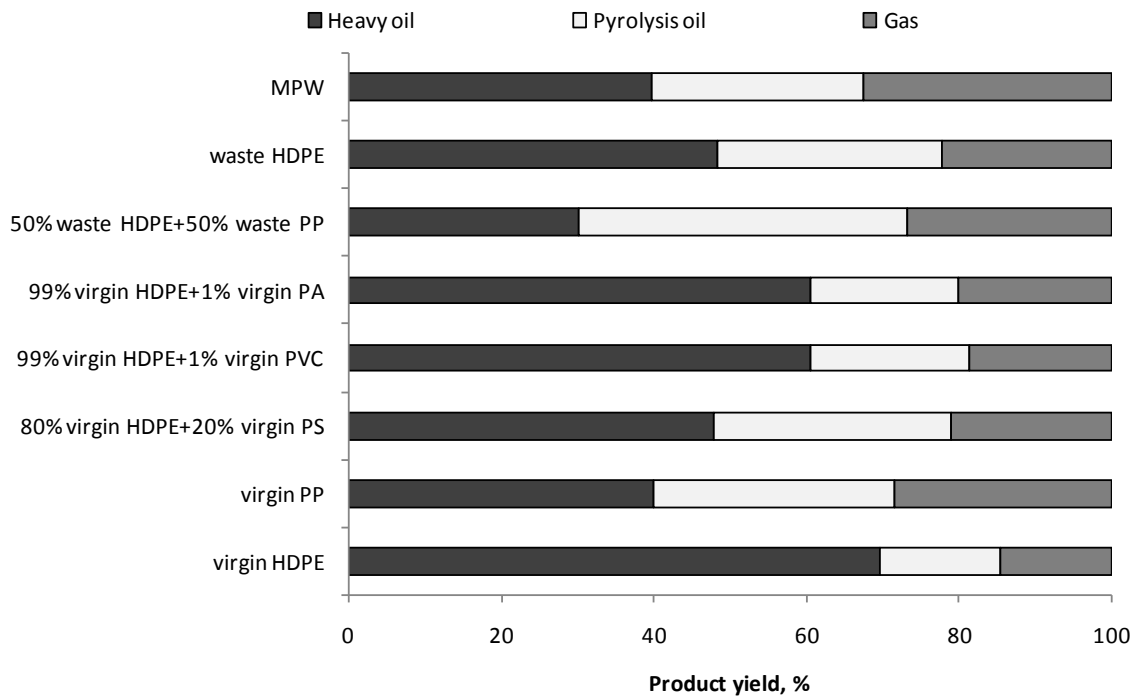
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Figure 1
Layout of the process



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Figure 2
Product yields obtained from plastic pyrolysis

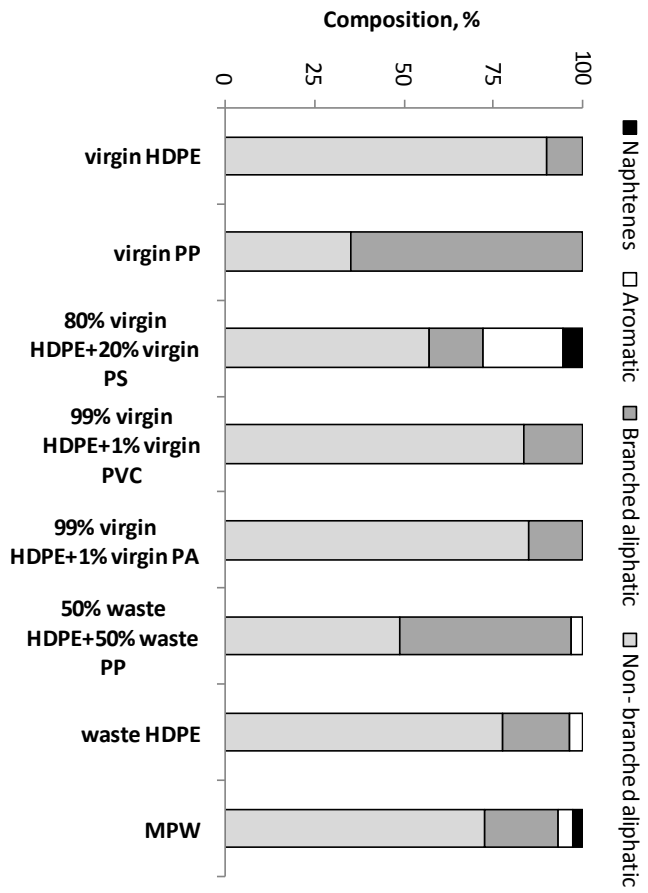


Figure 3
Composition of pyrolysis oils

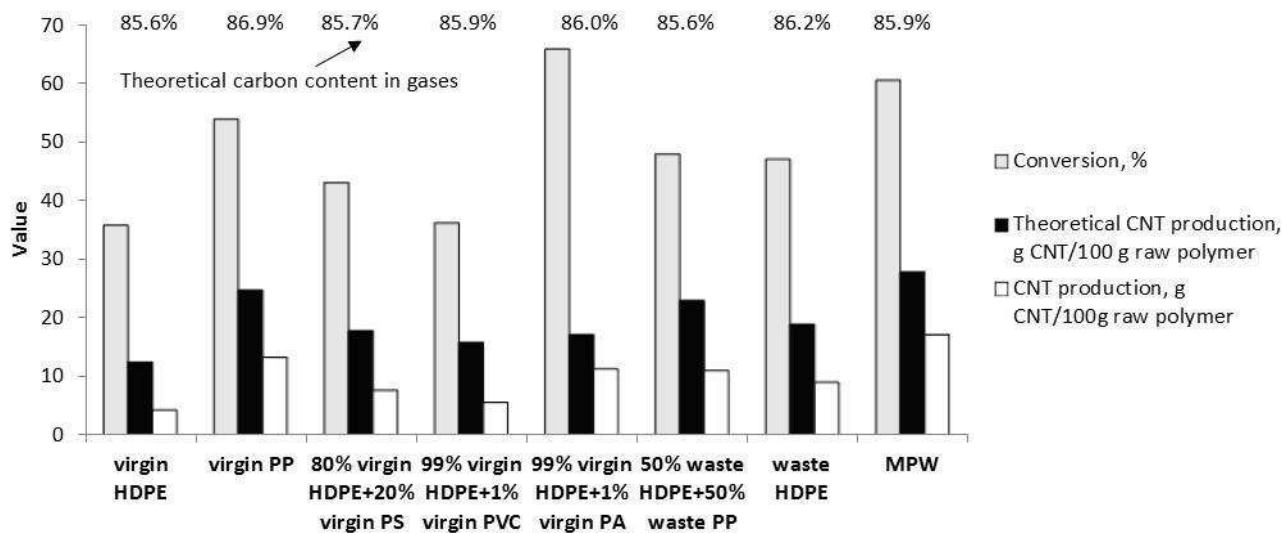
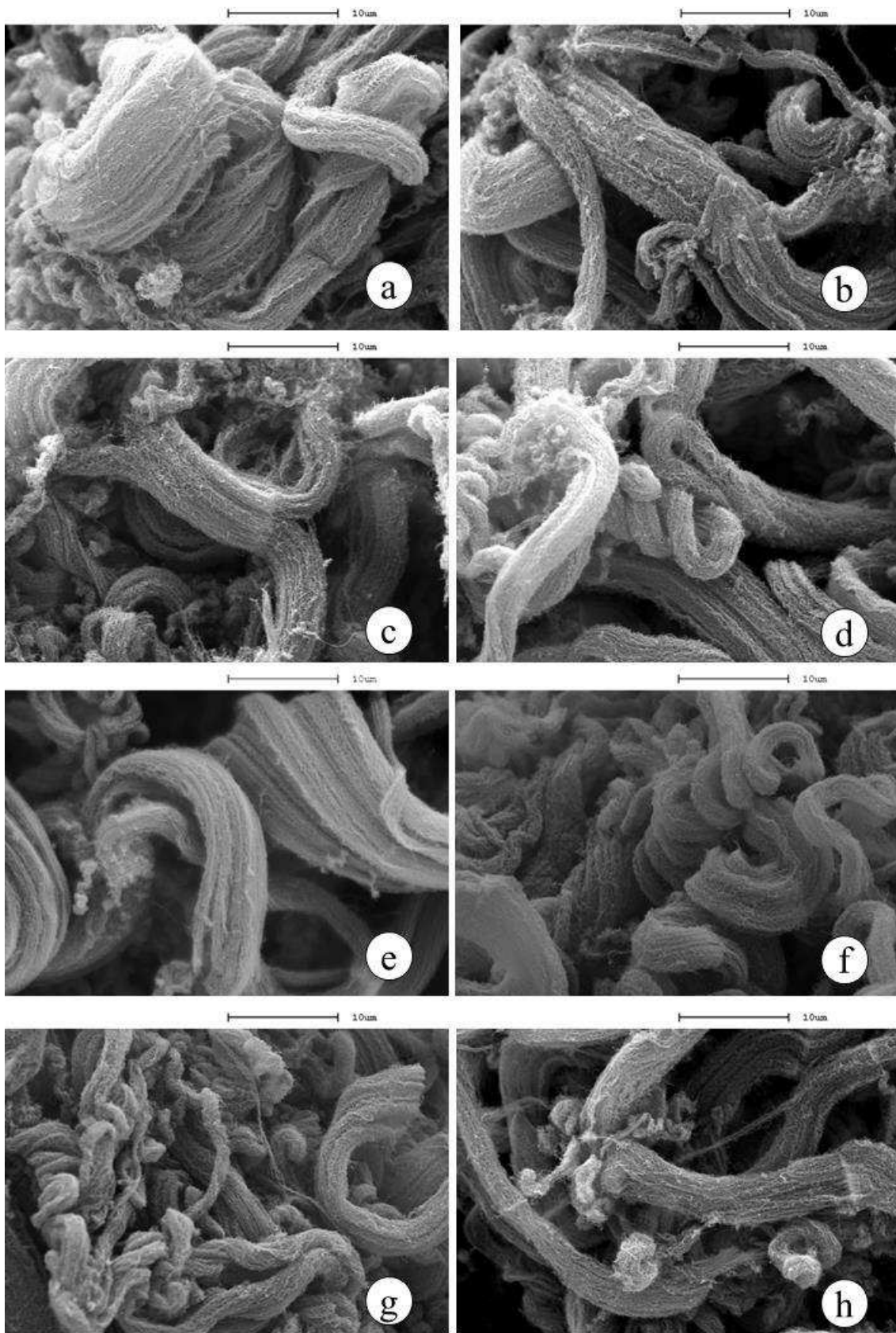


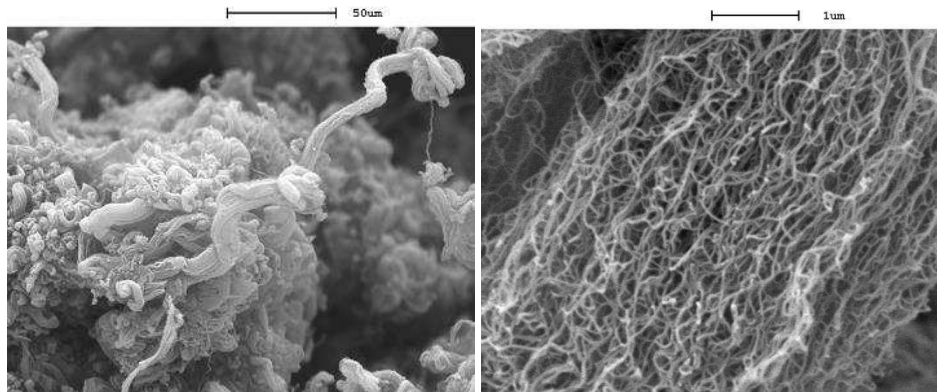
Figure 4
CNT production from gases

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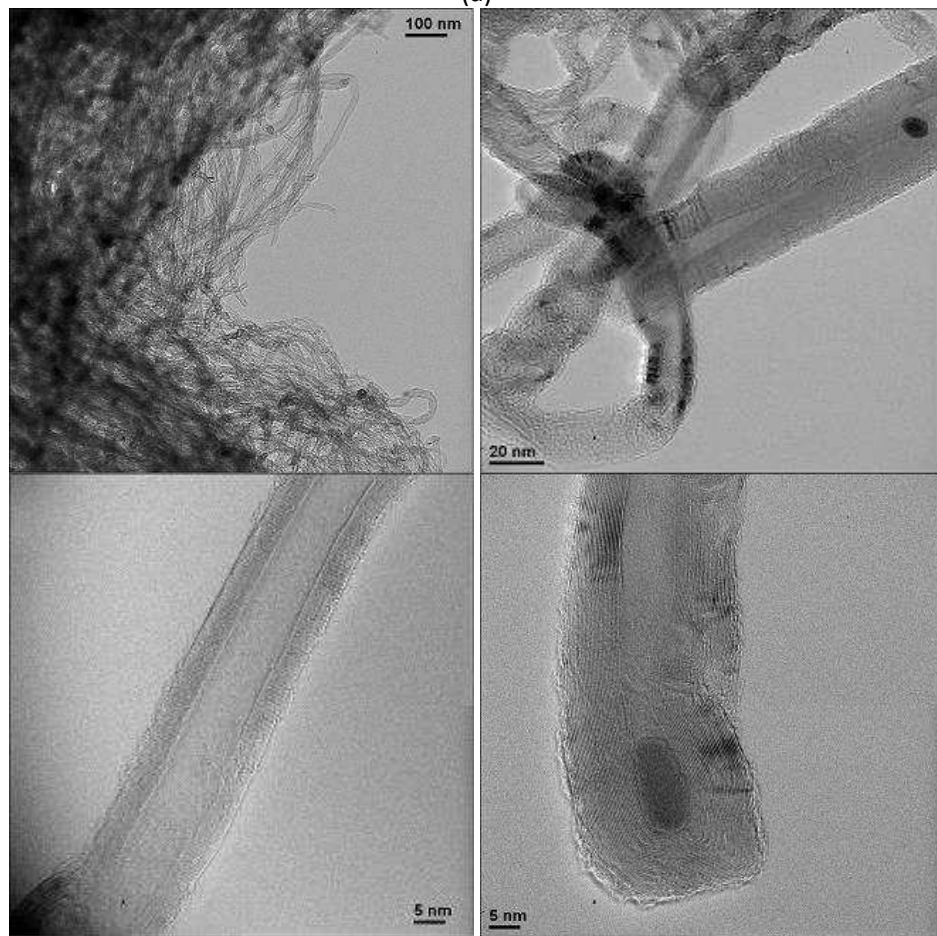
445
 446 **Figure 5**
 447 SEM micrographs of synthesized CNT
 448 ((a)-virgin PP, (b)-virgin HDPE, (c)- 80% virgin HDPE+20% virgin PS, (d)-99% virgin HDPE+1% virgin PVC,
 449 (e)-99% virgin HDPE+1% virgin PA, (f)- 50% waste HDPE+50% waste PP, (g)-waste HDPE, (h)-MPW)
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(a)



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(b)

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Figure 6
Typical SEM (a) and TEM (b) micrographs of synthesized CNT

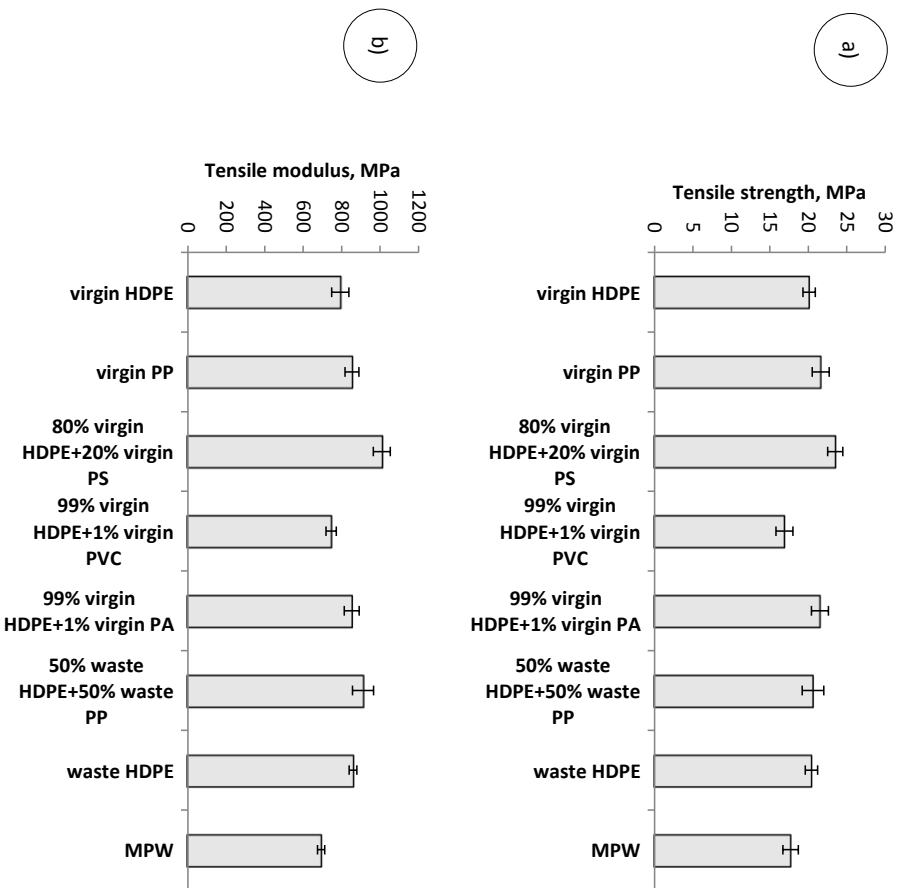


Figure 7 Tensile strength (a) and E-modulus (b) of CNT reinforced LDPE composites

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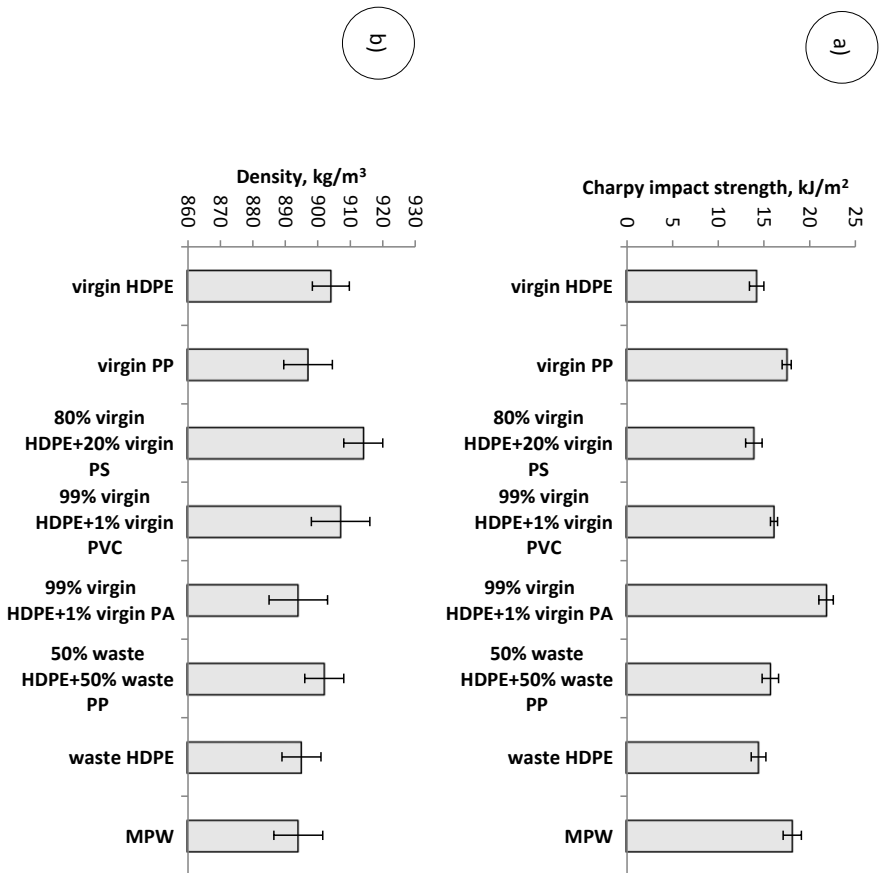


Figure 8 Charpy impact strength (a) and densities (b) of CNT reinforced LDPE composites

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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

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Table 2
The composition of gases obtained by plastic waste pyrolysis and their contaminants

Compounds	virgin	virgin	80% virgin	99% virgin	99% virgin	50% waste	waste HDPE	MPW	
	HDPE	PP	HDPE+20% virgin PS	HDPE+1% virgin PVC	HDPE+1% virgin PA	HDPE+50% waste PP			
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	
Contaminants	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

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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 oil	Colour	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow
	Density, g/cm³	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, mm²/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-

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