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Production and application of carbon nanotubes, as a co-product of hydrogen from the pyrolysis-catalytic reforming of waste plastic

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ABSTRACT

Hydrogen production from waste plastics is an important alternative for managing waste plastics. This work addresses a promising technology for co-producing high value carbon nanotubes (CNTs) in addition to the production of hydrogen; thus significantly increasing the economic feasibility of the process. Catalyst design is a critical factor to control the production of hydrogen and CNTs. NiMnAl catalysts, prepared by a co-precipitation method, with different metal molar ratios were developed and investigated using a two-stage fixed-bed reactor. It was found that the NiMnAl catalyst with the higher Mn content produced a higher yield of carbon (57.7 wt.%). Analysis of the carbon on the NiMnAl catalysts showed it to consist of ~90 wt.% of carbon nanotubes. The CNTs were recovered from the catalyst and added at 2 wt.% to LDPE plastic to form a composite material. The tensile and flexural strength and the tensile and flexural modulus of the CNT composite material were significantly improved by the addition of the recovered CNTs. Thus it is suggested that cost-effective CNTs could be produced from waste plastics as by-product of the production of hydrogen, enhancing the potential applications of CNTs in the composite industry.

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1. Introduction

Plastic is an essential material widely used in both everyday life and manufacturing processes since their commercial development in the 1930s and 1940s (PlasticsEurope, 2014). The proportion of plastic waste in municipal solid waste has increased significantly to now comprise around 10% of municipal solid waste (EU data) (Eurostat, 2015; PlasticsEurope, 2015). Currently, about 25 million tonnes of post-consumer plastic ends up as waste in the European Union

(PlasticsEurope, 2015), furthermore 38 wt.% of that plastic waste is disposed of in waste landfills representing a waste of resource. There is also growing recognition that waste plastics have a major impact on the environment, wildlife and human health, such as entanglement of marine animals and release of toxic chemicals from waste plastics (Thompson et al., 2009; Jambeck et al., 2015; Lee et al., 2015; Shah et al., 2014).

Therefore, there has been increasing interest into the development of new technologies for the recycling and recovery of waste

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plastics. Among the current technologies, advanced thermo-chemical processes including pyrolysis and gasification have shown the most promise (Acomb et al., 2014; Lopez-Urionabarrenechea et al., 2011; Straka and Bicakova, 2014). Compared to other technologies, in particular with combustion, pyrolysis/gasification has advantages of low emission of pollutants and high energy efficiency. Through pyrolysis, waste plastics can be converted into transportation grade liquid fuels (Lopez-Urionabarrenechea et al., 2011); gasification of waste plastics, can produce a hydrogen enriched syngas for producing energy, fuel and power (Acomb et al., 2013, 2014; Kannan et al., 2013; Straka and Bicakova, 2014).

Regarding the gasification of waste plastics, process efficiency and hydrogen production are key factors, which can be enhanced significantly by introducing a catalyst. Two stage pyrolysis–gasification/reforming has been investigated where the hydrocarbons resulting from pyrolysis are passed directly to a catalyst reactor in the presence of steam, where the hydrocarbons undergo steam reforming to produce a hydrogen rich syngas (Wu and Williams, 2009a). Catalyst research in such processes has centred on the formulation of catalysts which have highly efficient catalytic activity in terms of carbon conversion and hydrogen production. But also catalysts that exhibit high stability and that are not easily deactivated by coke formation on the catalyst surface. For example, it has been shown that hydrogen production from polypropylene is influenced by the type of catalyst support material used for the Ni-based catalyst and also the preparation method of the catalyst (Wu and Williams, 2009a). Also, the addition of noble metals such as ruthenium and platinum has been reported to significantly improve hydrogen production from the pyrolysis-catalytic steam reforming of waste plastics (Namioka et al., 2011).

Unfortunately, catalyst deactivation particularly by coke formation on the catalyst is a common issue for pyrolysis-catalytic steam reforming of waste plastics using Ni-based catalysts (Park et al., 2010; Wu and Williams, 2009b). However, an alternative research approach is to instead of developing catalysts for prohibiting coke formation, develop catalysts and process conditions to produce a higher value carbon product which can be recovered from the catalyst surface. For example, it has been reported that carbon nanotubes (CNTs) can be produced by manipulating process conditions during the processing of waste plastics (Nahil et al., 2015; Wu et al., 2014; Zhang et al., 2014). Therefore, unwanted coke formed on the surface of the catalyst is turned into a useful and valuable product – CNTs. One of the challenges for the further application of this technology is whether the product CNTs can be used for the production of industrial materials. For example, CNTs can be used as fillers for composite materials (polymers). Reinforced polymer is a common material used in many areas including aerospace, automotive and civil engineering application (Airbus, 2006). It has also been reported that CNTs reinforced polymers have higher strength-to-weight and stiffness-to-weight ratios compared with traditional carbon fibre reinforced polymer (Ansari et al., 2015; Song and Youn, 2006; Wuite and Adali, 2005). However, although the CNTs reinforced composite has enhanced mechanical properties compared with carbon fibre reinforced composite, the high cost of CNTs appears to prohibit the applications of CNTs and the use of CNTs-reinforced composite. The price of multi-walled CNTs is estimated (2013) to be between \$100 and \$25,000 kg⁻¹, depending on (Zhang et al., 2013). The costs need to be significantly reduced to match the cost and benefit for the industrial end-users. Thus, alternative routes for low-cost CNTs are required for promoting the deployment of related technologies.

In this work, we report on a promising route for converting waste plastics into a hydrogen-rich syngas and valuable carbon nanotubes, whose application as composite fillers was successfully demonstrated.

2. Materials and methods

2.1. Materials

Waste polypropylene (PP) with particle size around 1 mm was obtained from Regain Polymers Ltd. which was used for pyrolysis-catalytic steam reforming experiments. Low density

polyethylene (LDPE) was used for fabrication of composite, which was enhanced by CNTs produced in this work.

Ni-Mn-Al catalysts with Ni:Mn:Al molar ratios of 4:2:4 and 4:4:4 were prepared by a co-precipitation method. During the catalyst preparation, Ni(NO₃)₂·6H₂O, Mn(NO₃)₂·4H₂O, and Al₂(NO₃)₃·9H₂O (purchased from Sigma-Aldrich) were dissolved in deionized water. After the precipitation using NH₄OH solution, the suspension was stirred for an hour and then filtered under vacuum. The precursor was rinsed with deionized water, dried at 80 °C for about 12 h and followed by calcination at 800 °C for 4 h under static air with a heating rate of 1 °C min⁻¹. The catalysts prepared in this work were designated as NiMnAl 424 and NiMnAl 444.

2.2. Pyrolysis-catalytic steam reforming of waste plastics

Pyrolysis-catalytic steam reforming of PP was carried out in a two-stage reaction system. A schematic diagram of the system is shown in Fig. 1. The first stage was the pyrolysis of the PP, and the second stage involved catalytic steam reforming of the vapours derived from pyrolysis.

For each experiment, 1 g of waste plastic and 3 g of catalyst were placed inside the first and second reactor, respectively. The plastic sample was located inside a steel crucible, which was hung in the first reactor. The catalyst sample was supported by ~0.2 g quartz wool, which was placed on top of a perforated steel disc allowing gas to pass freely through. Nitrogen gas with a flow rate of 80 ml min⁻¹ was introduced throughout the experiment to provide an inert atmosphere, and also acted as an internal standard for gas analysis. The catalytic bed containing 1 g of catalyst was heated to 800 °C

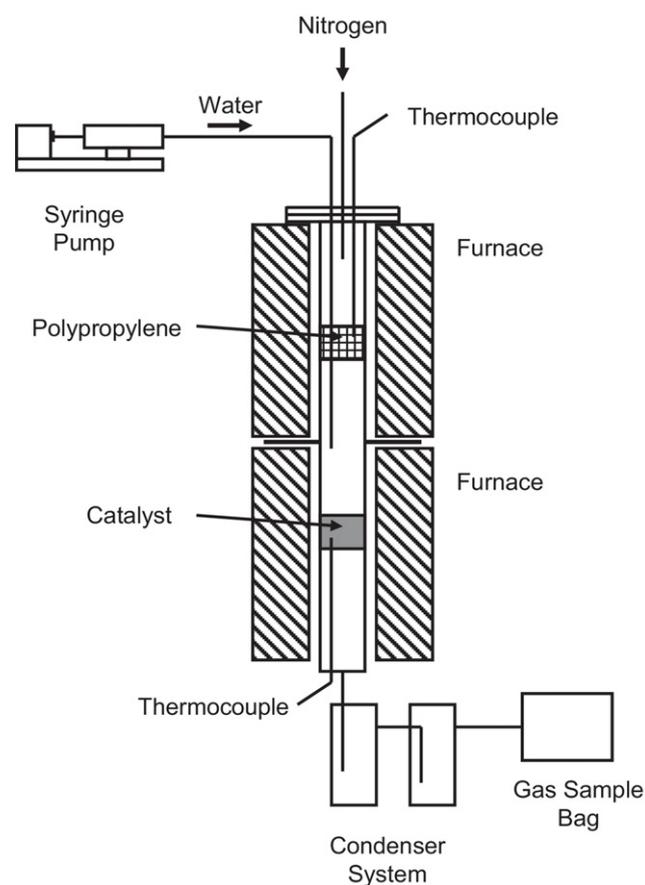


Fig. 1 – Schematic diagram of the reaction system.

Table 1 – Experimental results for pyrolysis-catalytic steam reforming of waste plastics using NiMnAl catalysts.

Items	Yield (wt.%)	
	NiMnAl 424	NiMnAl 444
Gas/PP	71.2	34.6
Carbon/PP	46.6	57.7
Pyrolysis residue/PP	7.0	6.3
CNTs/carbon	89.7	91.2
Mass balance	93.6	92.1
H ₂ production (mmol g ⁻¹)	56.6	37.2
Concentration (vol.%, N ₂ free)		
CO	16.56	9.08
H ₂	70.79	75.62
CO ₂	2.72	1.00
CH ₄	9.57	12.74
C ₂ –C ₄	0.36	1.56

initially. When the catalytic temperature was stable, the first stage where PP was placed was heated to 500 °C with a heating rate of 40 °C min⁻¹. Additionally, water was injected with a flow rate of 3.85 g h⁻¹ into the second stage to provide steam for catalytic reforming reactions. The complete experimental time was about 40 min. The experiments were repeated to ensure the reliability of the results. The derived products from the reactor were condensed using an air-cooled and a dry ice cooled condensation system, where liquid oil and unreacted water were collected. The non-condensable gases were collected using a Tedlar™ gas sample bag for further analysis. The gas yield and hydrogen production were calculated in relation to the weight of PP sample. The mass balance presented in Table 1 was calculated as the weight of products including gases, liquid (including non-reacted water) and pyrolysis residue, divided by the weight of the injected water and the plastic sample.

2.3. Gas analysis

Gases collected by the gas sample bag were analysed off-line by gas chromatography (GC). CO, H₂ and N₂ gases were analysed by a Varian 3380 GC with a 60–80 mesh molecular sieve column using argon as carrier gas. CO₂ gas was individually analysed by another Varian 3380 GC with a HayeSep 80–100 mesh column also using argon as carrier gas. C₁–C₄ hydrocarbon gases were determined with a further Varian 3380 GC using a flame ionisation detector with N₂ as carrier gas.

2.4. Characterisation of catalysts

The fresh catalysts were analysed by X-ray diffraction (XRD) on a Siemens D5000 between 10° and 70° with a scanning step of 0.02° using Cu K α radiation. The fresh and reacted catalysts and also recovered carbon nanotubes were characterised by scanning electron microscopy (SEM) (Hitachi SU8230) coupled with energy dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM) (FEI Tecnai TF20). The BET surface area of the fresh catalyst was determined by N₂ adsorption and desorption isotherms on a Quantachrome Autosorb-1. The results showed that the BET surface area for the NiMnAl 424 and NiMnAl 444 was 60.5 and 52.0 m² g⁻¹, respectively.

Temperature programmed reduction (TPR) analysis for the fresh catalysts was carried out using a Stanton-Redcroft thermogravimetric analyzer (TGA). During the TPR analysis, the

fresh catalyst was heated at 20 °C min⁻¹ to 150 °C and held for 10 min, then heated at 10 °C min⁻¹ to 900 °C using a mixture of 5% H₂ and 95% N₂ as carrier gas with a flow rate of 50 ml min⁻¹. The reacted catalysts and also the recovered carbons were characterised by temperature programmed oxidation (TPO) using TGA (Shimadzu) to obtain the amount of carbon deposition on the reacted catalyst and also the possible type of carbons e.g. amorphous or graphite. During the TPO, the sample (around 10 mg) was heated to 800 °C in air at a heating rate of 15 °C min⁻¹ and held for 10 min at 800 °C.

2.5. Fabrication and testing of low-density polyethylene based composite

The recovery of CNTs from the mixture of catalyst and carbons was carried out using aqua regia (nitro-hydrochloric acid mixture). The sample was dissolved in 100 ml of aqua regia (volume HNO₃:HCl volume ratio = 1:3) by refluxing in a round-bottomed flask for 3 h at 100 °C. The solution was allowed to be cooled to room temperature and the mixture was diluted with 100 ml of deionized water. The carbon was then filtered and dried at 105 °C overnight, and assigned as recovered CNTs. It is reported that surface functionalities of the CNTs would be influenced by the acid pre-treatment (Rosca et al., 2005). The effect of surface modification was not investigated in this work. Carbon nanotubes produced in this work have been tested as reinforcements in commercial virgin low density polyethylene (LDPE, Bralen RB 2-62, Tisza Chemical Group Public Limited Company, Hungary).

The matrix LDPE had the following properties: 11.4 MPa tensile strength, 7.5 MPa flexural strength, 348 MPa tensile modulus, 495 MPa flexural modulus, 18.2 kJ m⁻² Charpy impact strength and 155% tensile extension at break. 2% of CNT was added into the LDPE and reinforced composites were manufactured by a laboratory two roll mill (Lab Tech LRM-S-110/T3E, Labtech Ltd, Thailand). The temperatures of the rolls were 180 °C (first roll, n=20 rpm) and 150 °C (second roll, n=8 rpm). Then the composite samples were ground and 1 mm × 100 mm × 100 mm CNT reinforced LDPE sheets were press moulded using 180 °C with 15,000 psi pressure. The dimension of the specimens used for mechanical testing was 1 mm × 10 mm × 100 mm.

The tensile and flexural properties of the composite specimens were measured by a Instron 3345 universal tensile instrument. The cross head speed was 25 mm min⁻¹ both in the case of tensile and three point flexural tests. The temperature was 20 °C, while the relative humidity was 40% during the tests. The mean value of mechanical properties had been calculated based on five parallel independent measurements. CNT has a favourable effect in relation to the composite resistance against dynamic loading, therefore the Charpy impact strength was also measured by a CEAST Resil IMPACTOR. The software controlled instrument was equipped with a 4J hammer, while the specimens were not notched.

3. Results and discussion

3.1. Pyrolysis-catalytic steam reforming of waste plastics

Our previous work showed that after investigation of a large number of catalysts, NiMnAl based catalysts showed the highest performance in terms of both enhanced CNTs and

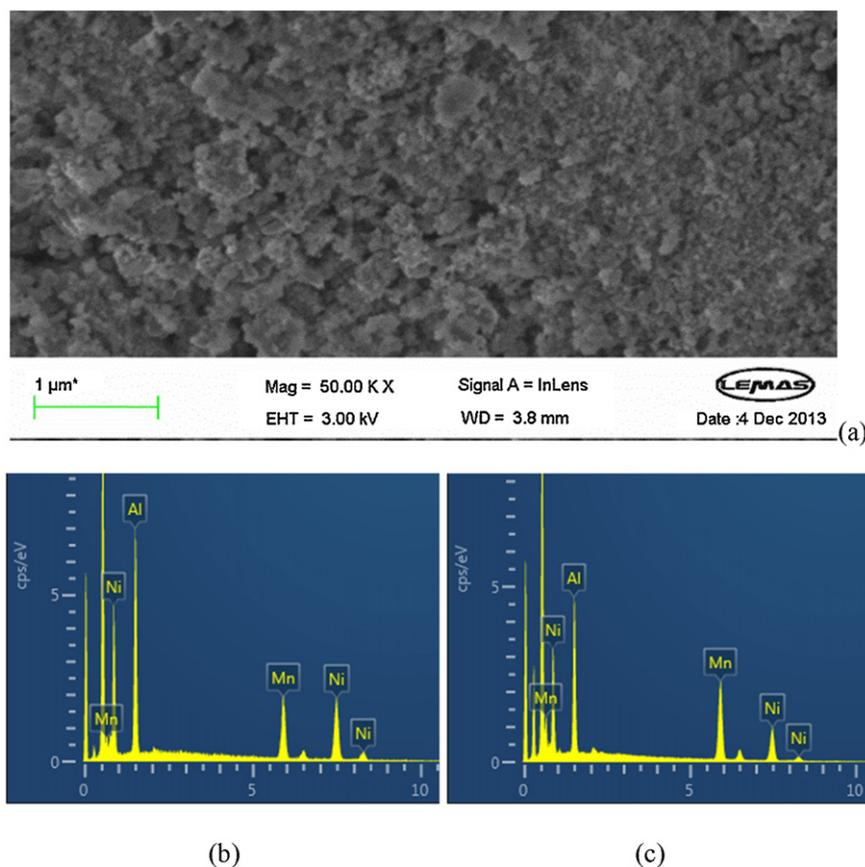


Fig. 2 – SEM-EDX results of fresh catalyst: (a) typical SEM micrograph; and EDX results of (b) NiMnAl 424 and (c) NiMnAl 444.

hydrogen production (Wu et al., 2014). Here we have investigated two NiMnAl catalysts with similar surface morphologies as identified by scanning electron microscopy (SEM) and analysis for the production of hydrogen. Energy dispersive X-ray spectroscopy (EDX) analysis confirmed that the content of Mn was higher in the NiMnAl 444 catalyst, compared with the NiMnAl 424 catalyst (Fig. 2). The results showed that the gas yield was reduced from 71.2 to 34.6 wt.% and hydrogen production from 56.6 to 37.2 mmol g⁻¹ sample, as shown in Table 1.

For the NiMnAl 444 catalyst, 57.7 wt.% of carbon yield was obtained. Cracking reactions (represented in Reaction (1)) might be promoted in the presence of the NiMnAl 444 catalyst, which resulted in a higher carbon formation and higher selectivity of H₂ (75.62 vol.%), compared with the NiMnAl 424 catalyst. NiMnAl 444 contained more Mn species, which have been reported to enhance carbon production during pyrolysis-catalytic steam reforming compared with other metals e.g. Mg, Ca and Ce (Nahil et al., 2015). Simultaneously, low molecular weight hydrocarbons e.g. CH₄ and C₂–C₄ have been produced with the NiMnAl 444 catalyst as shown in Table 1. Such gases would cause further catalytic steam reactions e.g. methane steam reforming (Reaction (2)), corresponding to the resultant higher ratio of H₂/CO. The existing Ni species on the catalyst surface were effective for reforming reactions (Sanchez and Comelli, 2014; Seo et al., 2011; Yoshida et al., 2015). The higher cracking ability of the NiMnAl 444 catalyst might be due to the presence of more reducible metal oxides, as shown from temperature programmed reduction (TPR) analysis (Fig. 3). Two major reduction peaks were observed from the TPR results, the first peak (around 470 °C) was assigned to the reduction of bulky NiO and MnO₂ particles, and the second peak at around 760 °C was assigned to the reduction of spinel phases. The

phases of NiO, MnO₂ and spinel were confirmed from the XRD analysis of the fresh catalysts (Fig. 4).



From Table 1, the carbon yield (produced on the catalyst) was increased from 46.6 to 57.7 wt.% with the increase of Mn content in the catalysts. It is noted that the carbons formed in the catalytic stage consisted of various types e.g. amorphous, filamentous and perhaps heavy hydrocarbons. Fig. 5(a) shows the morphologies of carbons accumulated on the catalyst surface (the figure shows a typical SEM micrograph, as there were only small differences between the reacted NiMnAl 424 and the reacted NiMnAl 444). It appears that many particles could be observed in Fig. 5(a), which might be part of the Ni-catalyst. After acidic washing (for carbon recovery from the catalyst),

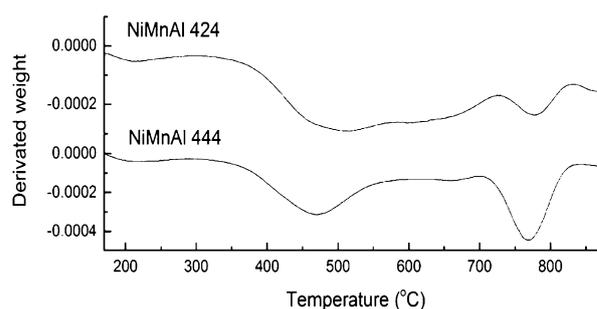


Fig. 3 – Temperature programmed reduction (TPR) of the fresh catalysts.

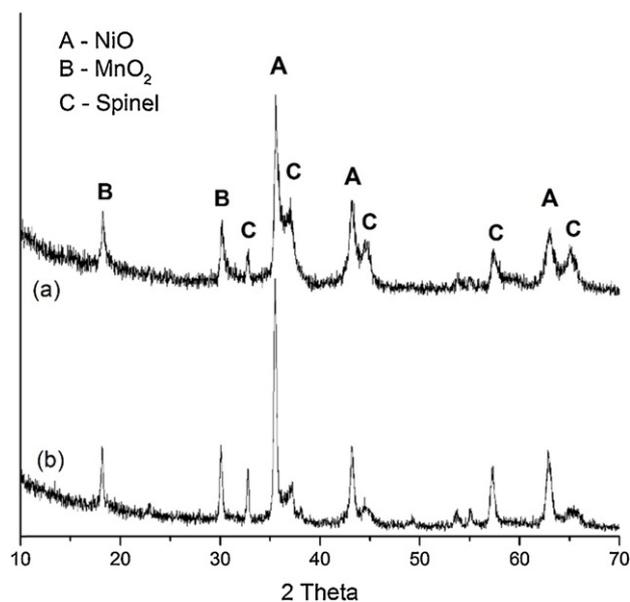


Fig. 4 – XRD analysis of the fresh catalysts: (a) NiMnAl 424 and (b) NiMnAl 444.

the recovered carbons were analysed again by SEM, and a typical micrograph is shown in Fig. 5(b); filamentous carbons with diameters around 30 nm could be clearly observed.

The carbon nanomaterials were further analysed by transmission electron microscopy (TEM), shown in Fig. 5(c), which confirmed the majority of carbon nanomaterials deposited on the catalyst were in fact carbon nanotubes. Fig. 5(d) shows an EDX spectra of the metal particles presented in Fig. 5(c), suggesting that Ni metal was responsible for the growth of carbon nanotubes in this work; Mn-based metal was not detected. Nickel is known to play an important role during the growth of CNTs through a tip-growth or root-growth mechanism (Kundrapu et al., 2012; Rao et al., 2014), while Mn has been

barely reported to participate in the growth of CNTs. Although Mn addition enhanced the CNTs production compared with other metals e.g. Ce (Nahil et al., 2015), here we suggest that Mn acted as a type of promotor for Ni-oriented CNTs growth. Catalyst promoters such as Mo have been reported to affect/enhance CNTs production (Li et al., 2004).

After recovering the CNTs from the mixture of catalyst and carbons, about 90 wt.% of carbons were obtained as CNTs as shown in Table 1. The oxidation properties of the recovered CNTs produced from the NiMnAl catalysts has been studied by temperature programme oxidation (TPO) as shown in Fig. 6. Around 10 wt.% metal residue (weight ratio of the residue after oxidation of the carbons) in the CNTs was observed; these metals might be contained inside the CNTs, which is known during metal-assisted CNTs growth. It should be noted that any metal residue inside the recovered CNTs were not removed prior to the application of the CNTs. A sharp oxidation peak on the TPO thermogram was found for the CNTs produced with the NiMnAl 424, suggesting that this CNTs product has a higher degree of uniformity although the CNTs yield using the NiMnAl 424 catalyst was lower than that derived from the NiMnAl 444 catalyst.

3.2. Carbon nanotube composite characteristics

Fig. 7 summarises the results of mechanical testing of the low-density polyethylene (LDPE) composite enhanced by the CNTs recovered/produced from the NiMnAl 424 and NiMnAl 444 catalysts. As the data demonstrates, the investigated CNTs have reinforced the composite, because enhanced mechanical properties are shown in the case of the CNT-LDPE composites compared with the virgin LDPE. The tensile and flexural strength of virgin LDPE were 11.4 and 7.5 MPa, respectively. In addition, the tensile strength was between 11.4 MPa (NiMnAl 444) and 13.1 MPa (NiMnAl 424) for the CNTs-LDPE composites, while the flexural strength was increased to 9.3 MPa (NiMnAl

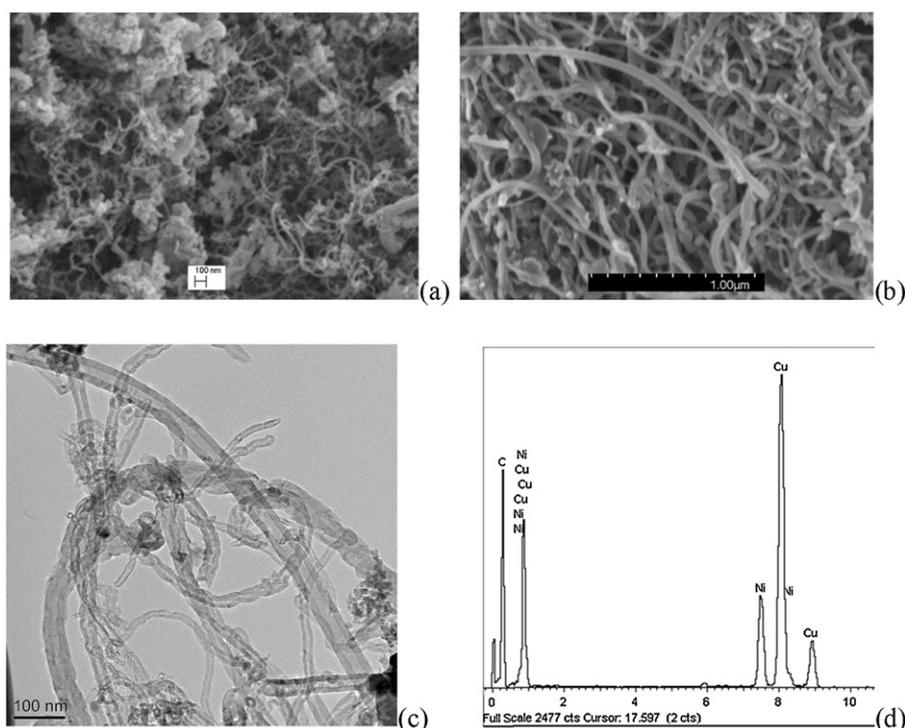


Fig. 5 – Morphologies of the reacted NiMnAl catalysts: (a) SEM of reacted catalyst; (b) SEM of recovered carbon; (c) TEM and (d) EDX of recovered carbon.

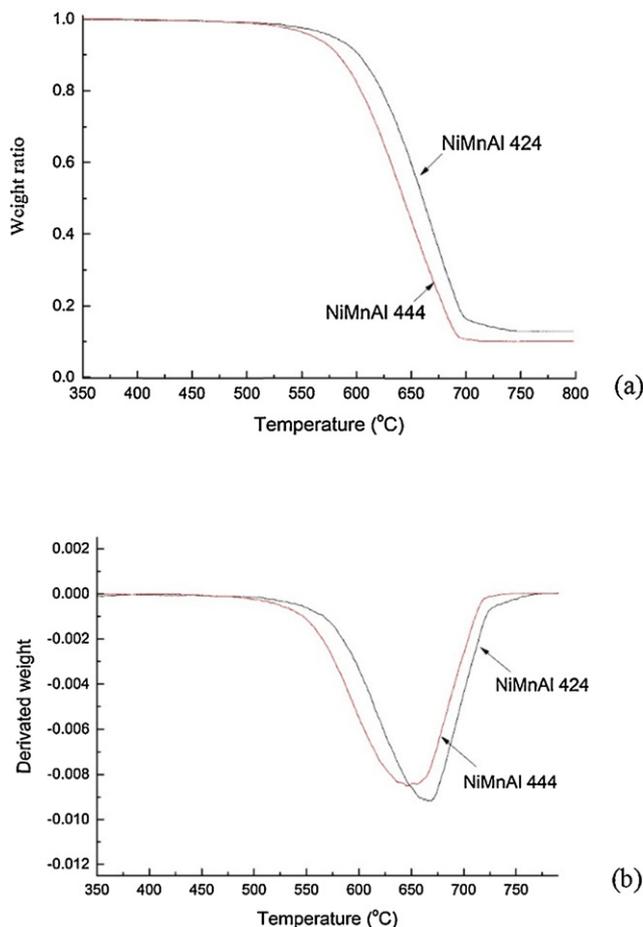


Fig. 6 – TPO of the recovered CNTs: (a) TGA results and (b) DTG derivative results.

424) and 8.4 MPa (NiMnAl 444), respectively. It is demonstrated that the tensile and flexural strength could be increased by 15% and 19%, respectively, using the CNTs produced from waste plastic using the NiMnAl 424 catalyst.

It is also clear that the CNTs-LDPE composites had developed much more stiffness, compared with the virgin LDPE used as the matrix of the composites. The relative elongation of virgin LDPE was 155% at break; in contrast it changed to between 10.0% and 10.6% using CNTs as reinforcements.

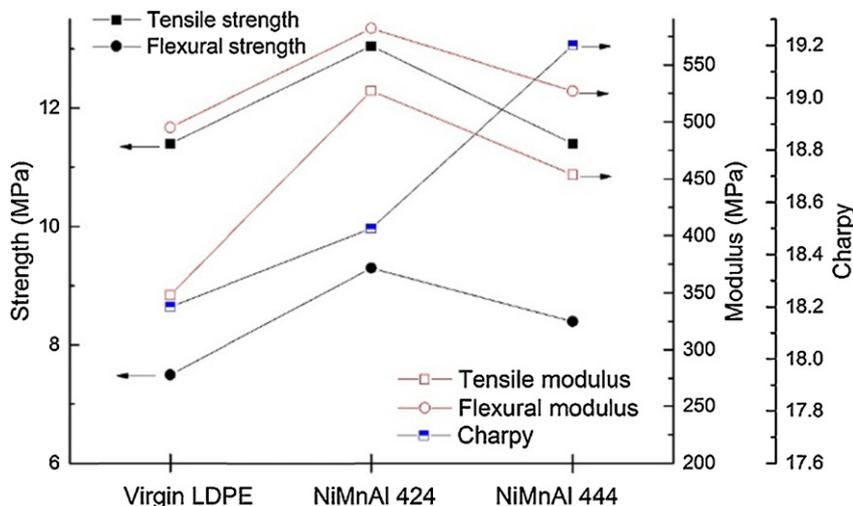


Fig. 7 – Mechanical properties of CNT-enhanced LDPE.

However, the elongations for the two CNTs-LDPE composites were very similar.

Both tensile and flexural moduli are important properties for composite materials, which are constants referring to the stiffness of the sample. It is calculated according to the Hooke-model, and is proportional to the mechanical strength and relative elongation of the sample. The matrix LDPE had a tensile modulus of 348 MPa and flexural modulus of 495 MPa. The tensile and flexural modulus were significantly higher in the case of the CNTs-LDPE composites (453.6–527.4 MPa for the NiMnAl 444 and 527.4–582.0 MPa for the NiMnAl 424, respectively). It indicates that the reinforced composites showed more stiffness, than the virgin LDPE.

One of the benefits of CNT reinforced composites is the high resistance against dynamic loading. Charpy impact strength is a widely used property for sample characterisation against dynamic loading. The Charpy impact strength of the CNTs-LDPE were between 18.5 and 19.2 kJ m² for the NiMnAl 424 and NiMnAl 444 derived samples respectively, while virgin LDPE had a Charpy impact strength of 18.2 kJ m², therefore Charpy impact strength could be increased by up to 10% by adding the produced CNTs into the LDPE composite.

As shown in Fig. 7, the CNTs-LDPE composite related to the NiMnAl 424 showed higher tensile and flexural strength, and also higher tensile and flexural modulus, compared to the composite related to the NiMnAl 444 catalyst. It is suggested that the higher strength and modulus corresponded to the better uniformity and higher crystallinity of the CNTs produced by the NiMnAl 424 catalyst (Fig. 7), although the CNTs-LDPE in relation to the NiMnAl 444 showed a much higher ability against dynamic loading. It has been reported that the presence of carbon agglomerates within the CNTs-composite reduced the tensile modulus of the composite (Bhuiyan et al., 2013). In addition, the non-homogeneous distribution of CNTs within the composite could also be responsible for the reduced modulus strength.

We propose the following mechanism for CNTs and hydrogen production from the pyrolysis-catalytic steam reforming of waste plastic (as illustrated in Fig. 8): (i) at the initial stage of the experiment, the catalyst has high catalytic activity for steam reforming of pyrolysis vapours to produce hydrogen and other gases; (ii) due to the saturation of carbon sources, carbon deposition on the surface of catalyst occurs; (iii) in this work, the NiMnAl 444 catalyst generated a large fraction of

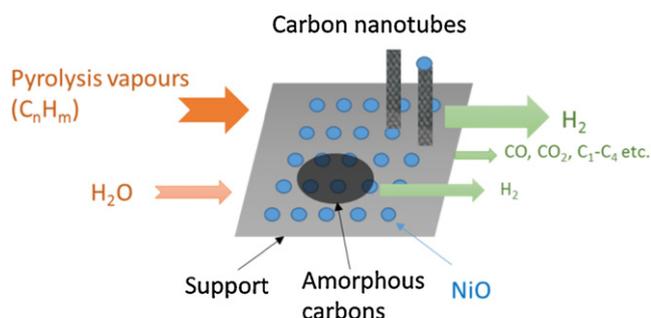


Fig. 8 – Schematic diagram of the proposed mechanism for hydrogen and CNTs productions from catalytic reforming vapours derived from pyrolysis of waste plastics.

amorphous carbons compared with the NiMnAl 424 catalyst due to the effect of promoter Mn. The amorphous carbons are known to encapsulate the reactive catalytic sites and reduce the catalyst reforming efficiency; as shown in Table 1, where the selectivity to CO (concentration) was lower and to CH₄ was higher for the NiMnAl 444 catalyst due to the prohibited reforming efficiency; (iv) CNTs formed on the surface of the catalyst has less of a negative effect on catalytic reforming compared with amorphous carbons, since reactants can still diffuse through the CNTs to contact with catalytic sites; (v) therefore, by controlling the process conditions, in this case, the design of catalyst, CNTs can be produced with little influence on hydrogen production efficiency. Due to the production of carbon, the water gas reaction for hydrogen production is limited, thus the total hydrogen yield was lower for the NiMnAl 444 catalyst (Table 1).

The promising process reported in this research enables the production of high value CNTs together with clean hydrogen energy carrier from waste plastics. This not only promotes the valorisation of waste materials and the development of a hydrogen economy, but also facilitates the applications of low-cost CNTs and the development of CNTs-enhanced composites. For example, it is estimated that 30 wt.% of waste polypropylene (~\$180 tonne⁻¹) can be converted into multi-walled CNTs (~\$20,000 tonne⁻¹), which are ready to be used as additives to composites, in addition to the production of ~900 Nm³ hydrogen per tonne of waste plastics. The price of multi-walled CNTs estimated in this work is based on the value (~\$100 kg⁻¹) reported in 2013 (De Volder et al., 2013). We have also demonstrated that adding only 2 wt.% of the produced CNTs to a LDPE composite, resulted in an increase in its flexural strength by about 20%, and Charpy impact strength enhanced by about 10%.

4. Conclusions

This work has demonstrated the co-production of valuable CNTs and clean hydrogen energy carrier as a promising process for the management of waste plastics. The influence of catalyst development and application of the produced CNTs as composite filler have also been reported. The results show that NiMnAl 444 catalyst produced a higher yield of carbon (57.7 wt.%), however containing a larger fraction of amorphous carbons compared with the NiMnAl 424 catalyst (46.6 wt.% carbon yield). Producing a high fraction of amorphous carbons also resulted in a lower efficiency of reforming reactions in relation to the low CO selectivity and high CH₄ concentration for the NiMnAl 444 catalyst. The addition of the produced CNTs (2 wt.%) to LDPE composite showed higher mechanical

strength compared with virgin composite. The product CNTs-composite related to the CNTs produced with the NiMnAl 424 catalyst showed higher tensile (13.1 MPa) and flexural strength (9.3 MPa), and higher tensile and flexural modulus, compared to the composite produced using CNTs related to the NiMnAl 444 catalyst (tensile strength: 11.4 MPa; flexural strength: 8.4 MPa). Thus, it is suggested that cost-effective CNTs could be produced from waste plastics together with clean hydrogen energy carrier. In addition, producing CNTs from waste materials could potentially promote the applications of CNTs in the field of composite production.

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