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# Evaluating the mechanical properties of reinforced LDPE composites made with carbon fibres recovered via solvothermal processing

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# Abstract

Carbon fibre was recovered from a thermoset composite via a solvo-thermal process and used as reinforcement in low density polyethylene (LDPE). The oxidized recovered carbon fibres have shown better properties than original non-oxidized fibres. The best interactions between the continuous and dispersed phases were found using 3-aminopropyl-trimetoxysilane and experimentally synthesized polyalkenyl-polymaleic anhydride based polymers. The tensile strength of the prepared composites nearly doubled when 3-aminopropyl-trimetoxysilane was used as compatibilizer, in comparison to the composites prepared without additives. Based on infrared analysis, a chemical reaction has been proposed between –COOH groups of compatibilizers and the –OH groups of the carbon fibre surface for the best composites.

Keywords: A. recycling; B, mechanical properties; C. mechanical testing

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#### 1. Introduction

Plastics and polymer-based composites have become dominant structural materials in engineering practice, with worldwide annual thermoplastic production in excess of 300 Mt [1, 2, 3]. Key sectors utilizing polymers and composites include aviation, construction, pharmaceutical, sports, civil engineering, automotive, packaging and medical devices. Carbon fibre (CF) is one of the most widely used reinforcements in order to improve the properties of plastics. The application of CF reinforced composites is increasing and the total demand of worldwide CF is around 100,000 tons per year [1]. One of the most important benefits of CF reinforcement is the significant increase in mechanical strength. However, the application of reinforcements can also cause disadvantages; e.g. the problem for recycling (or re-use) of end-of-life composite plastic wastes. Hence, despite the numerous advantages of reinforced plastics, the sustainable recycling of fibre reinforced polymers is an unsolved problem.

Pickering [4] reviewed the recycling technologies for thermoset composite materials. They concluded that in spite of the available processes, marketing and economic issues are the main difficulties affecting the recycling of reinforced thermoset composite materials. Similar conclusions were reached in the review published by Pimenta et al. [5], who gave a comprehensive overview about the existing plants for carbon fibre reinforced composite recycling, including the current status of existing and emerging technologies and summarized the potential structural applications of reinforced composites. In addition, Pimenta et al. [5] concluded that other non-technical and legislative issues must be solved for wider application of recovered reinforcements.

The most investigated options for reinforced plastic recycling are mechanical recycling, thermal processing (thermolysis, pyrolysis, gasification, etc.) and solvolysis. During mechanical processing, the waste materials are ground and then reincorporated in thermoset or thermoplastic resin or composites as filler or partial reinforcement depending on the recovered fraction. It has been suggested that mechanical recycling should be suitable only when the origin and composition of raw materials are known and if they are uncontaminated [4, 5]. Major issues with mechanical recycling include the formation of immiscible phases and the chemical and/or mechanical degradation of both reinforcements and polymer chains. Unfortunately, both issues are responsible for the significant deterioration of reshaped products obtained from mechanical recycling. Generally, mechanical strengths decrease with a subsequent decrease in the environmental/chemical resistance of mechanically recycled reinforced plastics [1-7].

Thermal and thermo-chemical processes are another option for recycling of reinforced plastics [8-13]. Among these processes, pyrolysis, gasification and hydrothermal processing have been investigated as technologies for recycling of solid wastes, such as waste composite materials. However, carbon fibre reinforced composites recycling using pyrolysis and hydrothermal processing can be potentially viable because these processes are seen as cost effective at the moment. Pyrolysis involves heating the waste material to elevated temperature (400-600°C) in the absence of air/oxygen, while gasification ( $T \ge 800$ °C) can be used to convert the organic components of waste into CO and H<sub>2</sub> in the presence of a limited amount of steam and air/oxygen [4, 11-13]. Under hydrothermal processing, water is used as a solvent [14-18]. The properties of water under hydrothermal conditions are distinct from those of ambient water. Some of these properties include much lower dielectric constant and higher ion products compared to ambient water, thereby giving water an apparent non-polar nature with the capability to dissolve nonpolar organic compounds. Sometimes, the solvating ability of water under these conditions can be improved by the addition of organic co-solvents such as alcohols. Liquid products of thermal processes contain a variety of organic compounds depending on the polymer type and the reaction conditions and can be used as raw material for chemical synthesis and as feedstock in refinery for petrochemicals or upgraded to fuels [15].

Depending on the fibre content of raw materials, thermochemical recycling can yield substantial solid residues containing mostly the reinforcement materials. Further cost effective and high-value applications of this solid fraction requires further investigation as some reinforcements are known to be costlier than the matrix (plastic) materials. Therefore, the recovery and re-application of reinforcements obtained from waste reinforced polymers appears a practical and attractive solution to this problem. On the one hand, re-using recovered CF is also of practical interest, because the demand for CF is currently higher than its production rate. On the other hand, the re-application of recovered carbon fibres depends on their mechanical strength and the improvement of interfacial force between the matrix material and the reinforcement surface. In practice, several methods are used to achieve better interfacial forces and decrease the interfacial tension. Furthermore, weak organic acid (e.g. acetic acid) solution or even alkali chemicals (e.g. NaOH, KOH) are also widely used for chemical modification of fibre surfaces [18-27]. Most often, organosilane compounds, MA-grafted organic fatty acid derivative, MA-grafted petroleum based polymers (e.g. MA-g-HDPE, MA-g-PP, etc.) are used as coupling agents or

compatibilizers [21, 22, 27]. The surface of polymer composites and compatibilizer efficiency could be also modified by oxidative effect [28].

In this work, recovered carbon fibre obtained from solvothermal processing of waste carbon fibre reinforced plastics (CFRP) was used as a reinforcement material from the production of reinforced low-density polyethylene (LDPE). The recovered CF was applied directly or oxidized in air prior to its application. The recovered CF was blended into the polymer matrix using commercial and experimentally-synthesized additive or compatibilizers.

#### 2. Materials and Methods

#### 2.1. Recovery of carbon fibre obtained from composite plastic waste

The waste CFRP sample was made of woven carbon fibre on a resin, which is used for making vehicle interiors. The CFRP sample used in this study was obtained from Milled Carbon Ltd, UK who recovers carbon fibres from end-of-life vehicles including automobiles and aircrafts. Thermogravimetric analysis of the CFRP sample revealed that it consisted of 61.5 wt% carbon fibre and 38.5 % resin. The resin was found to be of a polybenzoxazine backbone (a phenolic-type thermoset) [11]. The elemental (CHNSO) composition of the CFRP was; 80.3% carbon, 2.05% hydrogen, 5.9% oxygen, 4.15% nitrogen and 1.65% sulphur. The procedure for the recovery of the CF from the waste CFRP has been previously described [15]. Briefly, 10 g of the CFRP sample was loaded into a 500 ml capacity hydrothermal reactor, along with 50 ml ethylene glycol and 10 ml distilled water. This combination of water and ethylene glycol gave up to 96 wt% resin removal [15]. Figure 1 shows the SEM images of the recovered carbon fibres. However, the SEM images show that the surfaces of the recovered CF were covered by char residue, which agreed with the work of Wong et al. [29]. Therefore, a portion of the recovered CF was further cleaned by oxidizing in air at 250 °C for 1.5 h. Both the oxidized and non-oxidized recovered CF samples were re-used to make reinforced plastics in this work.

# 2.2. Materials for reinforced LDPE composites

The aim of the current work is to investigate the possibility of re-using recovered CF reinforcement in making new composite materials, such as reinforced LDPE (low density polypropylene). For this purpose, the recovered carbon fibres have been used as reinforcement in virgin, commercial LDPE

(Bralen RB 2-62, Tisza Chemical Group Public Limited Company, Hungary). Prior to the composite manufacturing, the matrix polymer was characterized as follows; the LDPE has 11.4 MPa, 7.5 MPa and 18.2 kJ m<sup>-2</sup> tensile strength, and flexural strength and Charpy impact strength, respectively. The melt-flow index was 2.2 g per 10 min (at 190°C, 2160 N), while the tensile and flexural modulus were 348 MPa and 495 MPa, respectively. The tensile extension at break of matrix material was 155% without reinforcement.

For reinforcing, three different kinds of carbon fibres have been used: recovered non-oxidized CF (as was obtained from solvo-thermal processing of waste CFRP), recovered oxidized CF and commercial un-sized CF (PANEX<sup>®</sup>33). The commercial CF has 3800 MPa tensile strength, 228 GPa tensile modulus, 1,81g cm<sup>-3</sup> density and approximately 7.2 µm diameter. In addition, the mechanical properties of the recovered CF were measured. The recovered CF has tensile strength, tensile modulus and density of 3904 MPa, 211 GPa and 1.75 g cm<sup>-3</sup>, respectively.

A loading of 15 wt% carbon fibre have been added into the virgin LDPE matrix in each case. Different surface modifying/coupling agents were tested to achieve stronger interfacial forces – and advanced mechanical properties – between the reinforcements and LDPE matrix. The main properties of the coupling agents/additives are summarized in Table 1.

In this study, two commercial and two experimental coupling agents have been used. The two commercial additives were, the mostly used silane type and MA-grafted-polymer, while the CFA-1 and CFA-2 experimental additives were polyalkenyl-polymaleic-anhydride derivatives, synthesized at the University of Pannonia. The applied concentrations were 1% for the commercial additive, and 2% for the experimental additives based on cost considerations, as the 2% concentration of experimental additives had been found to be more cost-effective than 1% of the commercial additive [23]. In addition, additive concentrations were set according to preliminary experiments and usually low additive concentrations are required. Based on earlier results, improved properties were observed for composites made of 2% experimental additives, while application of 1% commercial additive had shown the most advanced econo-mechanical properties [23].

## 2.3. Preparation of recovered carbon fibre reinforced LDPE composites

For composite manufacturing, a laboratory two-roll mill (Lab Tech LRM-S-110/T3E, Labtech Ltd, Thailand) was used. 15% carbon fibre was added into the virgin LDPE in each case. The temperatures of the rolls were 180 °C (first roll, n=20 rpm) and 150 °C (second roll, n=8 rpm). Firstly, the LDPE was placed on the heated rolls and then the reinforcement was added together with additives to the molten polymer. Following the composite preparation, they were ground into particles with dimensions up to 5mm using a laboratory grinder. Then 100mm x 10mm sheets were press-moulded at 180 °C using 5,000 psi pressure and then specimens with dimension of 1mm x 10mm x 100mm were cut from the carbon fibre reinforced LDPE composite sheets for further testing.

#### 2.4. Testing the properties of reinforced LDPE composites

Composite samples have been characterized in relation to their mechanical properties (tensile, flexural and impact properties). The mean value of each property has been calculated based on five parallel independent measurements. Tensile properties were determined using an Instron 3345 universal tensile machine using 90 mm min<sup>-1</sup> crosshead displacement rate. The fast cross head speed chosen for this work had been used previously in preliminary experiments and therefore allowed comparison of the results obtained from this present study and the preliminary experiments. During the tests, the ambient temperature was 23 °C, and the relative humidity was 35 % in all cases. Preloading was not applied. The three point flexural tests were performed by also the before mentioned Instron 3345 universal tensile tester. The crosshead displacement rate was 20 mm min<sup>-1</sup> in all cases.

A CEAST Resil IMPACTOR was used for Charpy impact strength measurement. The machine was equipped with a 4J hammer, while the specimens were not notched.

To identify the physico-chemical structure of samples, analysis was carried out at room temperature with Fourier Transform Infra-Red (FTIR) spectroscopy fitted with an Attenuated Total Reflectance (ATR) accessory (Ge crystal). The experiments were conducted on a TENSOR 27-type FTIR-ATR. The uniform number of 32 scans with resolution 3 cm<sup>-1</sup> was maintained in all cases. In addition, a scanning electron microscope (SEM) (LEO 1530) and a transmission electron microscope (TEM) (FEI Tecnai TF20) were used to study the surface morphology of the carbon fibres.

#### 3. Results and discussion

#### 3.1. Fibre/ash content analysis of manufactured composites

Regarding the effect of the additives and carbon fibres, the real fibre/ash content and its distribution inside the composite is a crucial question. Therefore the fibre/ash content was measured by MSZ EN ISO 3451-1:1999 method. In this method, the fibre/ash content of composite materials can be obtained by taking measurements at nine independent points over the composite sample to better understand the average fibre content of specimens. Crucially, results demonstrated that the average fibre/ash content of the reinforced composites was between 14.3% and 15.2%, while the deviation was between  $\pm 0.2\%$  and  $\pm 0.6\%$ . Thus, results confirmed that the uniform loading of 15% carbon fibres unto the LDPE was accurate and successful.

#### 3.2. Mechanical properties of composites

## 3.2.1. Tensile and flexural strengths

Table 2 summarizes the tensile and flexural strength of commercial non-sized carbon fibre, non-oxidized recovered and oxidized recovered carbon fibre containing LDPE composites. The mean values of the properties were calculated based on five parallel measurements and the standard deviation (SD) is also included in Table 2. It is clear that the RSD% values ((SD/Mean)\*100) values were all below 10% and less than 5% in most cases. In general, it can be seen that the commercial carbon fibre and recovered carbon fibre composites did not differ significantly without the presence of the additives (without any surface modifications): the tensile strength was between 12.7 MPa (commercial) and 17.4 MPa (oxidized), while the flexural strength were 7.5 MPa (non-oxidized), 7.9 MPa (oxidized) and 8.0 MPa (commercial). It is important to note, that the virgin LDPE matrix had 11.4 MPa and 7.5 MPa tensile and flexural strengths, respectively. The results suggest that the tensile property could be improved by the application of non-surface modified carbon fibre and the best results were found by the application of commercial 3-aminopropyl-trimetoxysilane. For instance, the tensile and flexural strength increased to 23.5 MPa and 16.9 MPa, respectively, using 15% non-sized commercial CF. With respect to the two experimentally-synthesized additives, CFA-2 resulted in higher composite strengths than CFA-1. By reinforcing the LDPE with commercial CF, the tensile strength of the reinforced LDPE composite was 20.1MPa with the CFA-2 coupling additive, while it was only 15.2 MPa with the CFA-1 additive

In general, LDPE composites containing commercial CF gave higher strength, than the other two kinds of recovered CF when the silane-type commercial additive was used. In other cases, the oxidized recovered CF appeared to give better performance that the commercial CF and the non-oxidized one. Therefore, lower tensile and flexural strengths were obtained from the use of non-oxidized recovered CF compared to the commercial CF. It is an important observation that neither tensile strength, nor flexural strength could be improved by chemical modification of the surface of the non-oxidized recovered CF. Indeed, the use of the additives (coupling agents) led to a lowering of both tensile and flexural strengths for the non-oxidized recovered CF compared to the properties of the oxidized recovered CF. The only exception was seen where the non-oxidized recovered CF gave higher tensile and flexural strengths compared to commercial CF in the presence of grafted-MA. This result could be attributed to favourable surface properties of recovered CF for anhydride or carboxyl groups present in grafted-MA. It is also clear from the results in Table 2 that the surface properties of recovered CF could be

significantly improved by oxidation. As mentioned earlier, the surface of the recovered reinforcement CF was generally covered by char residue [28] which could be unfavourable chemical groups for strong interfacial interaction. Such chemical groups could act as a barrier, thereby giving weak interactions that could not be improved by the coupling agents investigated in this work. Results showed that the unfavourable chemical structure of the CF could be modified by oxidation, because better chemical and/or physical linkage was established between the oxidized recovered CF reinforcement and the LDPE matrix. For instance, after oxidation, the tensile strength increased by 94%, 38%, 62% and 135% by the application of oxidized recovered CF compared to non-oxidized CF after the application of 3-aminopropyl-trimetoxysilane, grafted-MA, CFA-1 and CFA-2, respectively.

Table 2 also summarizes the tensile and flexural modulus of the composite specimens. The modulus is a widely used parameter for constructional material characterization, because it refers to the stiffness of material. According the results, the LDPE composites with commercial CF gave the highest modulus values and better results were obtained from the recovered CF after oxidizing.

# **3.2.2. Elongation at break**

The elongation at break was calculated by the change in specimen dimension in relation to the same dimension of the original specimen (Table 2). Results demonstrated that the presence of carbon fibres

significantly decreased the elongations, for example the matrix LDPE had 155% relative tensile elongation at break, which decreased to 2.37-6.72% for the commercial carbon fibre reinforced composites. Therefore the data show that the reinforced composites were much more rigid, than the virgin LDPE matrix. Commercial CF, non-oxidized CF and oxidized recovered CF had 3.22%, 4.07% and 4.10% relative elongation at break. Similar results have also been obtained by the application of 3aminopropyl-trimetoxysilane (2.37-4.01%) and grafted-MA (3.64-4.52%). Interestingly, the commercial CF coupled with the two experimental additives had elongations of 4.04% and 4.88%, while considerably higher values have resulted in the case of both recovered CF samples with the same additives (6.43-6.72%). Furthermore, the non-oxidized CF containing LDPE composites had a little higher relative elongation than that of oxidized CF.

# 3.2.3. Charpy impact strengths

Besides tensile and flexural properties discussed above, the resistance against dynamic stress is one of the most important mechanical properties of polymers. Generally, impact strength can give some predictions regarding specimen resistance against dynamic load. Table 2 shows the Charpy impact strength of carbon fibre reinforced LDPE composites. According to the earlier results, the matrix LDPE had 18.2 kJ m<sup>-2</sup> Charpy impact strength without reinforcement, which increased to 19.9, 23.0 and 26.7 kJ m<sup>-2</sup> using the commercial CF, non-oxidized recovered CF and oxidized recovered CF, respectively without any surface modification. Additives were favourable only in the case of the commercial CF, because the impact strength LDPE composites containing commercial CF changed from 22.9 kJ m<sup>-2</sup> (CFA-1) to 32.6 J m<sup>-2</sup> (3aminopropyl-trimetoxysilane). The application of recovered CF resulted in better impact properties than that of commercial CF without additives, whereas when coupling agents were used the LDPE composites with commercial CF gave the highest impact strength. The tested coupling additives could notably increase the impact strength of commercial CF-containing composites, more than recovered CF (both oxidized and non-oxidized) containing specimens. Although, the differences in the results for both commercial and oxidized CF were small, this could be attributed to the enhanced favourable surface properties of commercial CF. The impact strength of composites without coupling additives could be increased only in two cases: applying commercial 3-aminopropyl-trimetoxysilane in the case of oxidized recovered CF and CFA-2 experimental additive in the case of non-oxidized recovered CF.

#### 3.3. FTIR analysis

In order to investigate the theoretical coupling reactions, the manufactured carbon fibre reinforced LDPE composites were also analysed by FTIR-ATR. The spectrum of each sample shows many similarities between samples (Figure 2). For example, typical infrared spectral bands were found between 3000 and 2800 cm<sup>-1</sup>, where symmetric and asymmetric vibrations of both methyl and methylene groups gave sharp and intensive absorption bands. The next significant signals occurred at 1465 cm<sup>-1</sup> and 1260 cm<sup>-1</sup>. According to literature data, the peak at 1465cm<sup>-1</sup> was likely caused by C-O-H bending vibration of carboxylic acids and its derivatives, while the infrared signal at 1260 cm<sup>-1</sup> referred to the presence of C-O-C chemical linkage. Similar sharp, well isolated infrared bands were recorded at 1100 cm<sup>-1</sup> and 1015 cm<sup>-1</sup>. It is also well known that both infrared absorption bands should be attributed to the presence of ester or even ether groups. In addition, the very sharp and strong absorption band at 720 cm<sup>-1</sup> showed  $\beta$ (CH<sub>2</sub>) vibration.

# 3.4. Proposed LDPE-Additive-Carbon fibre ester linkage mechanism

By comparing the infrared results, it can be seen that especially, the intensities of hydroxyl group-related bands have changed significantly. Figure 3 shows the values of intensities of the infrared peak (log (I/I<sub>0</sub>)) at 1260 cm<sup>-1</sup>. Higher values of log (I/I<sub>0</sub>) at 1260 cm<sup>-1</sup> refer to more ester groups in the molecule, indicating bonding in the composites. Results of calculations refer to significant differences among the reinforced LDPE composites. Namely, the highest log (I/I<sub>0</sub>) values were found in the case of samples made using the commercial carbon fibre, while the lowest were found using non-oxidized recovered CF. However, better results were shown by oxidized recovered carbon fibres than the original recovered CF. It is important to note that a very similar tendency was found in the case of the infrared peaks both at 1100 cm<sup>-1</sup> and 1015 cm<sup>-1</sup>. According to this mechanism, the formation of more ester groups during the coupling was probably the cause of the higher values of log (I/I<sub>0</sub>).

Comparing Figure 3 with the results of mechanical testing (e.g. tensile test), it is also clear that better mechanical tests corresponded to higher  $log(I/I_0)$  values. Generally, it could be also concluded that the lowest values of log (I/I<sub>0</sub>) was obtained when non-oxidized recovered CF was used. However, those lower values could be significantly improved by the post-recovery oxidation procedure. Presumably, favourable

surface properties were obtained for the formation of chemical linkage between the additives and oxidized carbon fibre, especially via ester group formation.

The coupling effects of the silane-based and MA-grafted polymer type compatibilizers are well known. It has been described, that 3-aminopropyl-trimetoxysilane can link to the -OH groups on the carbon fibre surface via the Si-O-fibre chain [22, 27]. It suggest that the two other Si-O-CH<sub>3</sub> and Si-(CH<sub>2</sub>)<sub>3</sub>-NH<sub>2</sub> chains are free, and can participate in strong chemical linkage with the LDPE matrix. In essence, the carboxyl groups of MA-g-polymer type compatibilizers are able to chemically link to the -OH groups on the carbon fibre surface, while the long polymer side chain can physically interact with the non-polar LDPE matrix. Based on this theory, the two experimental additives can evolve a similar coupling mechanism. The applied experimental additives were low molecular weight polymers, with average molecular weights of 3000-5000g mol<sup>-1</sup>. Based on the infrared results, the proposed reaction scheme of coupling is summarized in Figure 4. In the structure of the compatibilizers, each monomer unit contains an anhydride ring with -CO-O-CO- chemical linkage. Another anhydride ring can react to produce an ester or half ester-type structure. The -CO-O-CO- chemical bonds were able to function as carboxylic acids. The possible chemical reactions between the experimental additive and carbon fibre should be through the reactions of the aforementioned -COOH groups of compatibilizers and the -OH groups of the carbon fibre surface. However, the most likely interaction between the two experimental coupling additives and the LDPE matrix was physical. As Table 1 demonstrates, owing to the half ester structure of CFA-2 experimental coupling agent, it could contain more carboxylic groups than the CFA-1additives. This could be the reason that the CFA-2 additive could establish more chemical bonds with the carbon fibre than the CFA-1 additive, as demonstrated by the mechanical tests in this study.

## 6. Conclusion

Carbon fibre reinforcement has been recovered by solvo-thermal processing of waste carbon fibre reinforced plastic material. The recovered carbon fibres have been re-used as reinforcements in LDPE polymer matrix in their oxidized and non-oxidized forms. It can be concluded that the oxidized carbon fibres showed better properties than the original non-oxidized sample. The surfaces of the recovered carbon fibre were modified by different chemicals, and the most advanced properties were found when commercial silane-based and CFA-2 experimental additive were used. Essentially, the tensile properties

could be improved by the two aforementioned additives. Based on infrared analysis, chemical reactions between the experimental additives and carbon fibre are proposed to be through the reactions of the – COOH groups of compatibilizers and the –OH groups on carbon fibre surface.

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# References

- Witik RA, Teuscher R, Michaud V, Ludwig C, Månson JAE. Carbon fibre reinforced composite waste: An environmental assessment of recycling, energy recovery and landfilling, Composites Part B 2013;49:89-99
- [2] Pimenta S, Pinho ST. The effect of recycling on the mechanical response of carbon fibres and their composites, Compos. Struct. 2012; 94(12): 3669-3684
- [3] Plastics the Facts 2013, An analysis of European latest plastics production, demand and waste data,
   Plastics Europe Market Research Group, 2013
- [4] Pickering SJ. Recycling technologies for thermoset composite materials current status, Composites Part A 2006; 37: 1206-1215
- [5] Pimenta S, Pinho ST. Recycling carbon fibre reinforced polymers for structural applications: technology review and market outlook, Waste Manage. 2011;31: 378-392
- [6] Cui J, Forssberg. Mechanical recycling of waste electric and electronic equipment: a review, J. Hazard. Mater. 2003; 99(3): 243–263
- [7] Dodbiba G, Takahashi K, Sadaki J, Fujita T. The recycling of plastic wastes from discarded TV sets: comparing energy recovery with mechanical recycling in the context of life cycle assessment, J. Clean. Prod, 2008; 16(4): 458–470

- [8] López FA, Rodríguez O, Alguacil FJ, García-Díaz I, Centeno TA, García-Fierro JL, González C.
   Recovery of carbon fibres by the thermolysis and gasification of waste prepreg, J. Anal. Appl.
   Pyrolysis 2013; 104: 675-683
- [9] Wang Z, Li XD, Ma J, Li GV, Hu TJ. Fabrication of multi-walled carbon nanotube-reinforced carbon fiber/silicon carbide composites by polymer infiltration and pyrolysis process, Compos. Sci. Technol. 2012; 72(3): 461-466
- [10] Schulte-Fischedick J, Zern A, Mayer J, Rühle M, Voggenreiter H. The crack evolution on the atomistic scale during the pyrolysis of carbon fibre reinforced plastics to carbon/carbon composites, Composites Part B 2007; 38(10):2237-2244
- [11] Nahil MA, Williams PT. Recycling of carbon fibre reinforced polymeric waste for the production of activated carbon fibres, J. Anal. Appl. Pyrolysis 2011; 91(1):67-75
- [12] Cunliffe AM, Williams PT. Characterisation of products from the recycling of glass fibre reinforced polyester waste by pyrolysis, Fuel 2003; 82,(18): 2223-2230
- [13] Cunliffe AM, Jones N, Williams PT. Recycling of fibre-reinforced polymeric waste by pyrolysis: thermo-gravimetric and bench-scale investigations, J. Anal. Appl. Pyrolysis 2003; 70(2):315-338
- [14] Oliveux G, Bailleul JL, Salle LGL, Lefèvre E, Biotteau G. Recycling of glass fibre reinforced composites using subcritical hydrolysis: Reaction mechanisms and kinetics, influence of the chemical structure of the resin, Polym. Degrad. Stab. 2013; 98(3):785-800
- [15] Yildirir E, Onwudili JA, Williams PT. Recovery of carbon fibres and production of high quality fuel gas from the chemical recycling of carbon fibre reinforced plastic wastes. J. Supercritical Fluids 2014; 92:107-114
- [16] Hyde JR, Lester E, Kingman S, Pickering S, Wong KH. Supercritical propanol, a possible route to composite carbon fibre recovery: A viability study, Composites Part A 2006; 37(11): 2171-2175
- [17] Dang W, Kubouchi M, Sembokuya H, Tsuda K. Chemical recycling of glass fiber reinforced epoxy resin cured with amine using nitric acid, Polymer 2005; 46(6):1905-1912
- [18] Oliveux G, Bailleul JL, Salle E. Chemical recycling of glass fibre reinforced composites using subcritical water, Composites Part A 2012; 43(11): 1809-1818

- [19] Meira AC, Castro MCS, Ribeiro J, Santos JP, Meixedo FJG, Silva A, Fiúza ML, Dinis MR, Alvim. Sustainable waste recycling solution for the glass fibre reinforced polymer composite materials industry, Const Build Mater 2013; 45: 87-94
- [20] Pickering SJ, Kelly RM, Kennerley JR, Rudd CD, Fenwick NJ. A fluidised-bed process for the recovery of glass fibres from scrap thermoset composites, Compos. Sci. Technol. 2000; 60(4): 509– 523
- [21] Jin GP, Wang XL, Fu Y, Do J. Preparation of tetraoxalyl ethylenediamine melamine resin graftedcarbon fibers for nano-nickel recovery from spent electroless nickel plating baths, Chem. Eng. J. 2012; 203: 440-446
- [22] Park SJ, Jin JS. Effect of Silane Coupling Agent on Interphase and Performance of Glass Fibers/Unsaturated Polyester Composites, J Colloid Interf Sci 2011; 242(1): 174–179
- [23] Miskolczi N, Szakacs H, Sedlarik V, Kucharczyk P, Riegel E. Production of Acrylonitrile butadiene styrene/High-density polyethylene composite from waste source using coupling agents, Mech Compos Mater 2014; 50(3):377-386
- [24] Wong KH, Pickering SJ, Rudd CD. Recycled carbon fibre reinforced polymer composites for electromagnetic interference shielding, Composites Part A 2010; 41: 693-702
- [25] DiBenedetto AT. Tailoring of interfaces in glass fiber reinforced polymer composites: a review, Mater Sci Eng A 2001; 302(1): 74–82
- [26] Bagherpour S, Bagheri R, Saatchi A Effects of concentrated HCl on the mechanical properties of storage aged fiber glass polyester composite, Mater. Des. 2009; 30: 271–274
- [27] Yu B, Jiang Z, Tang XZ, Yue CY, Yang J. Enhanced interphase between epoxy matrix and carbon fiber with carbon nanotube-modified silane coating, Compos. Sci. Technol. 2014; 99: 131-140
- [28] Żenkiewicz M, Rauchfleisz M, Czupryńska J, Polański J, Karasiewicz T, Engelgard W. Effect of electron-beam irradiation on surface oxidation on polymer composites, Applied Surface Science, 2007; 253: 8992-8999

[29] Wong KH, Pickering SJ, Turner TA, Warrior NA. Compression moulding of a recycled carbon fibre reinforced epoxy composite, SAMPE'09 Conference, 2009, Baltimore, MD, USA



Figure 1: SEM images of [A] Virgin; [B] Un-oxidized recovered; [C] oxidized recovered carbon fibres



Figure 2: FTIR spectra of manufactured composites (A: without additive, B: CA-1, C: MA-g-HDPE, D:

CFA-1, E: CFA-2)



Figure 3: Values of log  $(I/I_0)$  at 1260cm<sup>-1</sup>



Figure 4: The proposed reaction scheme of coupling between carbon fibre and commercial LDPE matrix

Sample ID	Appearance	Chemical structure	Supplier/Source	M <sub>w</sub> /M <sub>n</sub>
CA-1	Transparent liquid	CH <sub>3</sub> CH <sub>3</sub> O CH <sub>3</sub> O CH <sub>3</sub>	Aldrich Chemistry	179
MA-g- HDPE	Solid, granulates	O=C C=O	Viba Spa	n.a.
CFA-1	Yellow, honey-like dense liquid	$ \begin{array}{c c} & CH_{3} & \\ \hline & C & \\ \hline \hline & C & \\ \hline & C & \\ \hline \hline & C & \\ \hline & C & \\ \hline \hline & C & \hline \hline \\ \hline \hline & C & \hline \hline \hline \\ \hline \hline & C &$	Experimentally synthesized at University of Pannonia	7150/6520
CFA-2	Yellow, solid	$ \begin{array}{c c} & & & & & \\ & & & & \\ & & & & \\ \hline & & & &$	Experimentally synthesized at University of Pannonia	6345/5190

**Table 1:** The main properties of surface treating agents

		Without additive	3-aminopropyl- trimetoxysilane	MA-g- HDPE	CFA-1	CFA-2
Tensile strength, MPa	Commercial CF	12.7 (0.6)	23.5 (0.2)	13.2 (0.3)	15.2 (0.4)	20.1 (0.6)
	Non-oxidized CF	16.5 (0.4)	9.9 (0.5)	14.7 (0.4)	7.7 (0.2)	8.1 (0.2)
	Oxidized CF	17.4 (0.5)	19.2 (0.3)	20.3 (0.6)	12.5 (0.7)	18.9 (0.4)
Elongation at break, %	<b>Commercial CF</b>	3.22 (0.12)	4.01 (0.06)	3.64 (0.25)	4.04 (0.11)	4.88 (0.14)
	Non-oxidized CF	4.07 (0.25)	2.37 (0.17)	4.52 (0.09)	6.66 (0.17)	6.72 (0.11)
	Oxidized CF	4.10 (0.09)	3.08 (0.14)	4.44 (0.10)	6.57 (0.09)	6.43 (0.08)
Tensile modulus, MPa	<b>Commercial CF</b>	512 (42)	1150 (49)	541 (38)	451 (28)	971 (66)
	Non-oxidized CF	571 (37)	479 (35)	549 (26)	410 (19)	484 (38)
	Oxidized CF	663 (48)	966 (51)	899 (35)	509 (33)	912 (45)
Flexural strength, MPa	Commercial CF	8.0 (0.2)	16.7 (0.7)	6.2 (0.7)	6.5 (0.9)	11.9 (0.8)
	Non-oxidized CF	7.5 (0.4)	8.9 (0.3)	7.0 (0.5)	4.3 (0.2)	4.6 (0.3)
	Oxidized CF	7.9 (0.7)	15.4 (0.8)	11.7 (0.9)	6.1 (0.3)	15.8 (0.9)
Flexural modulus, MPa	<b>Commercial CF</b>	681 (36)	1415(59)	724 (42)	648 (25)	1118 (73)
	Non-oxidized CF	769 (48)	543 (31)	591 (26)	499 (17)	621 (41)
	Oxidized CF	755 (51)	1511 (62)	1015 (68)	647 (30)	1442 (37)
Charpy impact strength, kJ/m <sup>2</sup>	<b>Commercial CF</b>	19.9 (0.6)	32.6 (0.3)	23.2 (0.4)	22.9 (0.4)	26.6 (0.3)
	Non-oxidized CF	23.1 (0.4)	21.2 (0.5)	20.8 (0.7)	22.2 (0.2)	24.2 (0.4)
	Oxidized CF	26.7 (0.2)	28.2 (0.4)	21.7 (0.3)	16.3 (0.2)	25.7 (0.5)

Table 2: The average values of tensile, flexural properties and Charpy impact strength with standard

deviations