Surface treatment of recycled carbon fibre for interfacial enhancement in reinforced polypropylene product

A Salleh, N A Shuaib*, N W Y Omar and A I Azmi

Faculty of Engineering Technology, Universiti Malaysia Perlis, Uniciti Alam Campus, 02100 Padang Besar, Perlis, Malaysia

Email: norshahaizat@unimap.edu.my

Abstract. Recycled carbon fibre (rCF) is used in various applications as measures to reduce the carbon fibre waste in landfill. This study focuses on using rCF in powder form in injection moulded polypropylene (PP) products. The rCF was treated with 0.5 mol/L and 1.0 mol/L nitric acid. The tensile and flexural properties were evaluated and morphological surface of the samples was characterised using scanning electron microscopy (SEM). As the result, higher concentration of nitric acid increased the tensile strength but leads to lower flexural strength. Apart from that, the environmental assessment using OpenLCA software shows that the addition of RCF filler loading leads to reduction of climate change and acidification potential.

1. Introduction

Composite materials initially showed up in human artifacts [1]. The materials are being utilised everywhere from automobile, aerospace industry to the medicine, marine, energy and sports industry due to their excellent properties. From 2006 to 2016, the yearly worldwide interest for carbon fibre has expanded from around 16,000 tonnes to 72,000 tonnes and is estimated to ascend to 140,000 tonnes by 2020 [2]. This is because the carbon fibre has superior mechanical properties low weight, low thermal expansion, high stiffness, high temperature tolerance, high specific modulus and strength [3]. However, increasing use of carbon fibre reinforced plastic (CFRP) also increases the amount of CFRP manufacturing and end of life waste [4]. Excess carbon fibre waste in landfill is one of the environmental problems today.

CFRP, particular thermoset based products are hard to separate or recycle. Various technologies have been investigated to remove high value carbon fibre from CFRP [5]. The main recycling approach is to decompose polymeric matrices in different ways to make carbon fibre clean. The technology used to recycle CFRP can be classified into three main categories; mechanical, thermal and chemical recycling process [6].

The real challenge in using the recycled carbon fibre in new matrix is to increase interfacial bonding between them. It is known that the mechanical properties of a composite can be enhanced when bonding property between the reinforcement and the matrix is improved. Surface treatment is one of decent ways to deal with enhancing the bonding system between the fibre and the matrix [6]. Surface treatment on fibre is carried out to enhance the interfacial quality, for example, coupling agent treatment, sizing, warm medications, whiskerisation and wet oxidation. These surface adjustment techniques either improve the number of reactive functional group or increasing of the fibre to build the physical bonding with the matrix. The coupling agent treatment such as nitric acid is one of the most widely recognised techniques for fibre surface treatment [7]. Nitric acid treatment was found to
enhance the measure of oxygen-containing functional group on carbon fibre surfaces and to build the surface roughness in light of the development of longitudinal hole [3].

Polypropylene (PP) has emerged as an environmentally friendly polymer material as high chemical resistance coupled and low cost with high-end fabrication, high flexibility in applications and reusing. PP is normally protecting material in the thermoplastic gathering with a few points of interest including shorter moulding time, the ability to melt and have lower costs than thermoset polymers [8]. High embodied energy and material cost of virgin carbon fibre are issues to be considered [4]. Therefore, the usage of recycled carbon fibre not only minimise the cost, but also reduce the overall environmental impact of carbon fibre based product.

Based on previous work, there are many studies conducted on analytical experiments and fabrication processes incorporating rCF as fillers in plastic composites. Previous studies mostly focused physical and mechanical properties of the product. However, less study focuses on surface treatment of carbon fibre followed by investigation on product mechanical properties and environmental impact. This study investigates effect of differences in surface treatment conditions and on interfacial bonding between PP matrix and rCF. Besides, the environmental assessment of this treatment, which is rarely found in literature, is considered in this study.

2. Methodology

2.1 Raw materials
The raw materials used were rCF supplied by ELG Carbon Fibre Ltd, United Kingdom and polypropylene as thermoplastic matrix, was supplied by Sheng Foong Plastics Sdn Bhd in Perak, Malaysia. Nitric acid solution was used as chemical treatment for RCF. The solution was used to improve the measure of oxygen containing functional group of carbon fibre surface and build the surface roughness in light of the development of longitudinal hole.

2.2 Surface treatment
Before the surface treatment, rCF was sieved to obtain size particle of 150 µm. Surface treatment of rCF was carried out through a chemical process using two different concentration of nitric acid. The concentrations used were 0.5 mol/L and 1.0 mol/L. Table 1 shows the formulation of concentration nitric acid. RCF was immersed in nitric acid solution for an hour. Then, RCF was soaked and washed repeatedly with distilled water until the pH value changed to 7.

| Sample | Concentration of nitric acid (mol/L) | Nitric acid (ml) | Distilled water (ml) |
|--------|-------------------------------------|-----------------|---------------------|
| 1      | 0.5                                 | 6.25            | 193.75              |
| 2      | 1.0                                 | 12.5            | 147.50              |

*Nitric acid concentration = 16 mol/L

2.3 Composites fabrications
The composites were prepared by feeding the 10 wt% of rCF and PP pellets in a twin-screw LabTech extruder machine. The mixture compound was extruded and the strands were chopped into pellet form. All the specimens were injection molded into dumbbell-shaped tensile test bars and flexural test bars. The composite samples were fabricated according to ASTM standards.
2.4 Tensile testing
Tensile testing of the samples was performed according to ASTM D638 using Shimadzu Universal Testing Machine. The machine was equipped with Trapezium X software to carry out the tests. Four samples were tested for each composition and the average data was recorded. The specimen shape was the dumbbell-shaped type with the dimension size of 60 mm × 20 mm × 100 mm.

2.5 Flexural testing
The flexural testing was carried out following ASTM D683 standard using a Shimadzu Universal Testing Machine. The samples were in rectangular shape with a dimension of 124 mm x 12 mm x 3 mm (length x width x thickness).

2.6 Fourier transforms infrared analysis
Fourier transform infrared spectroscopy (FTIR) involves absorption of infrared radiation by a sample which results in several molecular vibrations by the chemical bonds of molecular compounds. In this study, FTIR Analysis model Perkin Elmer Spectrometer was used to characterise chemical changes on the surface of rCF from the chemical surface treatment process using attenuated total reflection (ATR) method. The baselines of the obtained spectra were corrected, smoothed and analysed with the SpectraGryph spectroscopy software.

2.7 Scanning electron microscopy
The surface morphology of the composites was observed using Scanning Electron Microscope (SEM) Hitachi TM 3000. The observation was done on cross-section of selected fractured specimen from tensile testing. The microscope produces details images of a sample by scanning the surface with a focused beam of electrons.

2.8 Environmental assessment
In this study, the main purpose of environmental assessment is to assess the product and process by considering essential information on energy consumption and material inputs. The assessment was done using OpenLCA software and data from experimental works. The CML Baseline as impact category was selected for this study. The impact categories such as a global warming potential, acidification and eutrophication were considered.

3. Results and discussions

3.1 Tensile properties
3.1.1. Tensile strength
The tensile strength of all composite products is presented in Figure 1. The result shows tensile strength increases significantly when rCF is added to PP. However, the value of tensile strength of the composite with treated rCF gradually decreases from 0.5 mol/L treatment to 1.0 mol/L treatment. This can be attributed to high oxidation, which occurred on the fibre surface. The primary reason for the reduction originates from the inappropriate processing conditions, which lead to excessive oxidation, and partially damages the fibre structure.

3.1.2. Tensile modulus
Figure 2 shows the modulus of elasticity of PP/RCF and PP/RCF(HNO3) composite at different concentration nitric acid. The figure shows a sharp increment of modulus of elasticity when PP reinforced with 10 wt % of rCF. Nonetheless, the result shows reduction of modulus of elasticity for treated rCF. This is cause by the low oxidation influence the modulus of elasticity on the sample with chemical treatment on rCF. Larger error bars for treated RCF composite shows that there is high variation and inconsistency in the data. The highest value of the modulus of elasticity is for untreated product. This proves that the addition of rCF significantly enhanced the modulus performance of the
pure PP. This is due to the incorporation of more rigid carbon fibre in the PP matrix [9]. By further sizing, the tensile strength should become more stable, while the modulus and elongation remain constant [10].

3.2 Flexural properties

3.2.1. Flexural strength

Figure 3 shows the effect of the untreated and treated RCF on flexural strength of the composites. The figure illustrates that the flexural strength increases from pure PP to PP + 10 wt % RCF (untreated) but there is a decline in flexural strength on PP + 10 wt % RCF + 0.5 mol/L (HNO₃) to PP + 10 wt % RCF + 1.0 mol/L (HNO₃). Flexural strength reduction could be due to over etching, which caused by high surface roughness. This tends to lower the penetration of matrix into pitting and cause decrease in bond strength between fibre and matrix. As a result, there is a reduction in stress transfer from matrix to fibres. The highest value of the flexural strength is the composite with PP + 10 wt % RCF (untreated). This improvement could be due to the etching process, which causes obvious pitting and roughness of the fibre surface. The existence of roughness tends to enlarge interlocking surface area between fibre and matrix which encourage stress transfer from matrix to carbon fibre and finally increase flexural strength [11]. But the flexural strength obtained in this study shows a declined value. This is caused by the treatment did not sufficient as to create roughness required.

3.2.2 Flexural modulus

Figure 4 shows the effect of the untreated and treated RCF on flexural modulus of the composites. From the graph, it can be seen that the flexural modulus increases significantly from pure PP to PP + 10 wt % RCF (untreated). The introduction of nitric acid (HNO₃) decreases the flexural stiffness of the composite. This is caused by the fibre surface roughness, which takes an important role in increasing the bond strength between fibre surface and matrix. However, the excessive roughness reduces the bond strength due to the existence of height regions formed on fibre surface, which prevents the penetration of matrix to the depressions on fibre surface. The result is in agreement with finding in a study by Ahmed et al [11].
3.3 Fourier transform infrared analysis

FT-IR spectra of carbon fibre have many peaks which related to existence of CH2, C–O, C–H, C=O, and C≡N bonds. Figure 5 shows FTIR spectra for RCF, RCF (0.5 HNO3), and RCF (1.0 HNO3). According Wenzhong et al [12], absorption peak is observed at 1627 cm\(^{-1}\) on the spectrum of the rCF etched by nitric acid, which is attributed to the C¼O stretching vibration of carboxyl group. Meanwhile, another broad absorption band at 3435 cm\(^{-1}\) is assigned to the presence of hydroxyl group. This indicates that the rCF was activated. The peaks in Figure 5 (a) and (b) show values which have not reached the wavelength, because of the use of weak concentration of nitric acid during surface treatment of the carbon fibre.
3.4 Surface morphology analysis

Scanning electron microscopy (SEM) analysis was used to examine the surface treatment of untreated and treated rCF. It is important to mention that the changes of surface treatment affect the interfacial adhesion. Figure 6 shows the images from SEM of rCF surface before and after the chemical treatment. It can be clearly observed that nitric acid treatment increased surface roughness and etching more transversely oriented along the fibre axis, compared to the untreated rCF. The increased roughness was seen followed by the presence of acidic functions (carboxylic and phenolic hydroxyl groups) [13]. These are introduced on the carbon fibre surface by nitric acid. Thus, this type of oxidation increases the total acidic functions while simultaneously increasing the surface area or roughness.

Figure 6. SEM images, a) untreated RCF, and b) RCF treated in 1.0 mol/L nitric acid

Figure 7 shows the SEM micrographs of tensile-fractured specimen of rCF composites. As shown in Figure 7 (a), a significant difference in fracture morphology can be observed. At x500 magnification, the fibre surfaces appear rough and surrounded by a layer of polymer. All these indicate that a good adhesion has been achieved. However, it is also noticed that the degree of polymer coverage on the pulled-out fibres and their adhesion with the host matrix depends on the surface treatment and loading. Plastic deformation of the host matrix is also very different from that of the sample without surface treatment and again the appearance varied with the type of coupling agent. The dependency of fracture morphology on coupling agent type will affect the composite mechanical performance [9]. It was analysed, the surface roughness of CFs has been shown to affect the fibre-resin bonding in composite materials [14]. The difference is observable based on the results in Figure 7 (a), where the sample is more brittle in its fracture behaviour in comparison in (b) and (c) as it is more ductile. Fibre pull out can be observed to be present in (c) and this signify that the bond is not properly formed with the fibre matrix for the composite sample with 10 wt % rCF resulting to its low strength.
3.5 Environmental assessment

The environmental assessment for PP/RCF and PP/RCF(HNO₃) composite was carried out using openLCA software. In life cycle inventory analysis, data in the form of energy and material flows and emissions released to the environment are aggregated. In this study, the results of this impact assessment are used for comparison of the pure thermoplastic product and composite with untreated and treated with nitric acid.

The environmental analysis for the PP/rCF composite on climate change potential and acidification potential are demonstrated in Figure 8 and Figure 9, simultaneously. It can be seen that the pure PP has higher climate change potential and acidification potential, compared to the other composite. That is because, the pure PP contains of 100% plastic. The higher use of plastic means high embodied energy hence the carbon dioxide emission. Meanwhile, the lowest carbon dioxide emission is the composite with PP + 10 wt % rCF with a value of 1.7819 kg CO₂eq. This composite contains 90 wt % of plastic while the remaining 10 wt % is the rCF, which assumed to have zero environmental impact. From this finding, it can be clearly seen that the usage of recycled filler of fibre could reduce environmental impact particularly for climate change and acidification potential.
Figure 8. Climate change potential for pure PP, untreated PP/RCF and PP/RCF(HNO$_3$)

Figure 9. Acidification potential kg SO$_2$ eq for pure PP, untreated PP/RCF and PP/RCF(HNO$_3$)

Figure 10 shows the eutrophication potential for PP/RCF and PP/RCF(HNO$_3$) composite. Eutrophication is one of the causes of the deterioration of water quality. From Figure 10, it can be observed that the increase of concentration nitric acid from treatment 0.5 mol/L to treatment 1.0 mol/L into PP matric increases the eutrophication potential. By using chemical treatment, the waste of the chemicals leads to high toxicity in the soil. Therefore, surface treatment of RCF using chemicals need to consider the disposal chemical waste to prevent high level of eutrophication.

4. Conclusions
This study investigates the effect of different concentration of nitric acid on polypropylene/recycled carbon fibre (PP/RCF) composite. The recycled carbon fibre (RCF) used in this study acts as inorganic filler reinforcement in the PP polymer matrix. From the results, the higher concentration nitric acid during the surface treatment, leads to higher tensile strength and elongation at break, but lower modulus of elasticity. For the flexural properties, higher nitric acid concentration leads to lower value of flexural strength and modulus of elasticity. The scanning electron microscope (SEM) analysis shows that the treatment of nitric acid on rCF shows changes on the fibre surface particularly on the roughness. Meanwhile, for the environmental analysis by OpenLCA software, it can be seen that the usage of RCF filler can be reduce climate change potential and acidification potential. However, the eutrophication level increases drastically with the usage of nitric acid for surface treatment.
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