Surface analysis of glass fibres using XPS and AFM: case study of glass fibres recovered from the glass fibre reinforced polymer using chemical recycling

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Abstract. In this study, we present the results of an experimental study of the use of the X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) to characterise the coatings of the recovered E – glass fibres. The recovered E – glass fibres were obtained using chemical recycling process coupled with ultrasound cavitation. The objective of this study was to analyse the impact of chemical recycling and the ultrasound cavitation process on the sizing properties of the recovered fibres. We obtained the recovered fibres and sized using 1 wt% 3 – aminopropyltriethoxysilane (APS). Part of the sized fibres was washed with acetone and analysed all the sample fibres using AFM and XPS. Results showed the different composition of sizing after extraction using acetone. We compared the results of this study with that of virgin clean glass fibres.

1. Introduction
Reinforced plastics (FRP) have been utilised in various industrial sectors due to the exceptional mechanical and physical properties as well as the chemical resistance that guarantees its durability during exploitation [1]. Thanks to these properties, the global production and utilisation of FRP as well as the reinforcing elements (fibres) have been increasing as shown in the statistics reported elsewhere [2][3]. As it is known from the famous idiom that there are two sides of the same coin, the implication of this idiom could be applied to the FRP and the properties thereof. The physical-mechanical properties as well as chemical properties mentioned above provide additional advantages during exploitation process and hinder recycling – reuse or disposal processes during the decommissioning processes of FRP wastes [2][4]. Consequently, FRP waste processors have resorted to several disposal/recycling methods to treat the end – of – life FRP wastes such as landfilling, mechanical and thermal treatment methods [5]–[9]. The literature mentioned above have provided detailed information on the implications of using these methods of disposing of waste FRP.

As countries focus on developing the ‘zero waste’ economy, the need for sustainable recycling of waste across various industrial sectors is growing. A similar trend is evident in the waste FRP (glass and carbon fibre reinforced polymer) sector. Researchers have considered and researched on the chemical recycling as one of the effective recycling methods: this is evident based on the recent publications.
focussed on the chemical recycling of both the glass and carbon fibre reinforced plastics [10]–[16]. Results from the publications mentioned above have shown the effectiveness of recovering of resin and reinforcing fibres based on the products analyses conducted. The quality of products is an essential factor in as far as any recycling process is concerned, and this is evident in the product analyses presented in the publications mentioned before. Suffice to say that the interfacial properties, just like the mechanical properties, are essential in determining the applicability of any fibre as a reinforcing element [17], [18]. The X-ray photoelectron spectroscopy and atomic force microscopy are useful techniques for analysing the interfacial properties and topography of the fibres and has been used by many researchers [17], [19].

In this experimental study, we used chemical recycling method and utilised the ultrasound process. Ultrasound cavitation, like other known mechanochemical processes, is inherent in the intensification process of any chemical reaction. The ultrasound cavitation created by the ultrasound equipment is inherent in increasing the temperature of the solvent thereby reducing the overall energy demand and reducing the overall time required for the chemical recycling process. In light of the additional advantages of the using the ultrasound cavitation, the motivation of this study was to analyse the effect of the chemical recycling and ultrasound process on the interfacial properties of the recovered glass fibres. This study is part of continuous research focussed on developing a mechanochemical – enhanced recycling process for different fibre reinforced polymers.

2. Materials and Methods

2.1. Glass fibre recovery process

The material used in this study was the glass fibre reinforced polymer (nonwoven fibre). Figure 1 shows the chemical recycling process workflow used for the recovery of the glass fibres.
The depolymerisation process was conducted in a reactor equipped with a solid probe of the high-power laboratory ultrasound apparatus (Sonics VC – 750) and a heating mantle to provide necessary heat. The sample GFRP (sample size 30 mm X 30 mm X 8 mm) was washed several times with pressurised water to remove impurities from the surface. Later on, the sample was immersed in the solvent (Benzyl alcohol, reagent grade) for 10 minutes followed by the depolymerisation process. The process mentioned above was undertaken for 60 minutes, and the temperature of the solvent increased from the initial temperature of 100°C to 170°C due to the ultrasound cavitation process.

The liquid products from the depolymerisation process were separated using the laboratory vacuum filtration apparatus to extract the glass fibres and undissolved polymer resin. The glass fibres and undissolved resin were poured into a beaker with ethanol (reagent grade) and shaken thoroughly for 24 hours. Later on, the glass fibres were removed and dried at room temperature. The process and solvents used in the mentioned above were based on the principles proposed by [11]

2.2. Glass fibre sizing procedure

We used the sizing procedures written in other research papers [20]–[23]. The recovered glass fibres were soaked in acetone for 24 hours after which we washed them thoroughly with water. The fibres were sized with 1 wt% 3 – aminopropyltriethoxysilane (APS) solution for 15 minutes: this solution was prepared by hydrolysing an equivalent amount of the APS in deionised water and stored it at room temperature for one hour. After sizing, the samples were desiccated and dried in a vacuum oven for 6 hours at a temperature of 50°C. Later on, part of the glass fibres was selected and immersed in acetone at room temperature for 24 hours. Subsequently, the samples were dried in a vacuum oven at a temperature of 50°C for 2 hours. All the samples were prepared according to the specification of the atomic force microscopy (AFM) and the X-ray photoelectron spectroscopy (XPS).

XPS was carried out using Quantera SXM (ULVAC- PHI Inc., USA) at a take-off angle of 45°. This analytical equipment had a monochromatic x-ray source (Al - Kα) and highly focused beam (<9 microns). AFM was carried out using XE – 70 model AFM supplied by Park instruments. The AFM had a TESP cantilever from Bruker Nano and was operated at room temperature in atmospheric air condition and a scan speed of 0.4 Hz. The Scan area was approximately 10 x 10 μm. The 256 x 256 pixel images and the mean surface roughness of the sized fibres were processed using XEI version 4.3.2 software (Park Systems). The root means surface roughness of the fibres was determined using the formula proposed by Liu et al. [20].

3. Results and discussion

3.1. XPS analysis of sized fibres

Figure 2 shows the XPS wide spectra of the recovered fibres sized with 1 wt% APS. The elements chosen for analysis were aluminium, boron, carbon, calcium, magnesium, nitrogen, oxygen, sodium and silicon. These elements were analysed and results presented by other authors [20], [22] and shown in Table 1. For comparison analysis, we used the data from other publications [20], [22], [24]. The normalised surface compositions/ratios were calculated based on the Silicon element (Si) according to the information provided by Thomason [24]. Thus, we calculated the C/Si, N/Si and O/Si ratio as shown in Table 3. Results showed a higher carbon concentration than the concentrations presented by the Liu et al. [20] and Zhuang et al. [22]. In previous research, Liu et al. [20] attributed the higher than anticipated values to possible contamination on the surface of the glass fibres. Even though there’s evidence of contamination, it was possible that the overall layer of the sizing was weak and the thin layer of the sizing left some part of the surface exposed. These contaminations were also seen in the AFM images (below) and were attributed to the quality of the fibres recovered and the post-recovery treatment
process thereof. Other publications revealed that the recycling process might negatively affect the interfacial properties and this might influence the layer of the sizing [2], [13]. For example, Okajima et al. [13] conducted XPS analysis on unsized carbon fibres and indicated that the peak areas of the functional groups from recovered carbon fibres were smaller than those of the virgin carbon fibres.

Results from the study mentioned before might characterise the lower than expected interfacial properties. While reviewing the existing composite recycling processes, Thomason et al. [2] noted that the thermal-based treatment processes might negatively influence the properties of the recovered fibres (e.g., strength loss).

Table 1. The atomic composition of the surfaces of recovered glass fibres sized with 1 wt% APS.

| Element | Recovered glass fibres sized with 1 wt% APS | Liu et al. [20] | Zhuang et al. [22] | Thomason [24] |
|---------|--------------------------------------------|----------------|-------------------|---------------|
| Al      | 3.5                                        | 3.3            | 3.6               | 1.8           |
| B       | 1.1                                        | 1.3            | 1.2               | 0.8           |
| Ca      | 2.9                                        | 1.7            | 4.0               | 2.0           |
| C       | 35.3                                       | 34.0           | 30.4              | 39.8          |
| Mg      | 0.8                                        | 0              | 1.2               | -             |
| N       | 3.8                                        | 5.7            | 2.2               | 0.8           |
| O       | 37.5                                       | 38.0           | 39.9              | 39.8          |
| Si      | 14.8                                       | 15.7           | 15.4              | 15.3          |
| Na      | 0.3                                        | 0.3            | 0.2               | -             |

Note: Data presented by Liu et al., Zhuang et al. and Thomason et al. were for virgin glass fibres.
Thomason et al. [24] showed that the reduction in fibres’ properties exhibited a linear inversely proportional relationship with the treatment/conditioning temperature. Thus, higher temperatures and extended treatment period characterised with the chemical recycling method using the ultrasound cavitation might have reduced the properties of the recovered fibres in this experimental study. High-power ultrasound cavitation is a source of energy which is released into the solvent and the FRP through the collapse of the cavitation bubbles. After immersing the sample in acetone, a significant amount of the hydrolysed silane layer was extracted. Experimental results presented by Thomason [24] showed a 75% extraction of sizing on the glass fibre. Nørgaard et al. [21] indicated that the extraction process might remove 90% of the APS sizing. The extraction was attributed to the removal of free amino groups and weakly chemisorbed compounds [20]. Even though the amount extracted might be at the rates mentioned above, the quality of the fibres obtained after recycling process might have led to the lesser than expected thin layer of sizing on the surface of the recovered glass fibres. Therefore, it is possible that a more significant proportion of the sizing (because of the less sizing) and in particular the strong chemisorbed compounds might have been extracted when immersed in acetone. The atomic concentration for the recovered glass fibres sized with 1 wt% APS and extracted using acetone are shown in Table 2.

Table 2. The atomic composition of the surfaces of recovered glass fibres sized with 1 wt% APS and extracted using acetone

| Composition, % | Al  | B   | Ca  | C   | Mg  | N   | O   | Si  | Na  |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|               | 4.2 | 1.3 | 2.8 | 22.5| 1   | 1.9 | 49.0| 17.1| 0.2 |

Table 3 shows the normalised ratios for the recovered fibres sized with 1 wt% APS prepared in this experimental study. From the table, it was evident that the C/Si and the N/Si ratios derived from our experimental analysis decreased while the O/Si ratio increased. The C/Si ratio was lower than the threshold value (10). The normalised ratio derived from our experimental study differed with the ratios obtained by other authors. We also observed that the C/N ratio in our experiment increased after acetone extraction and differed from the observations made by Liu et al. [20].

Table 3. Normalised ratios for the recovered glass fibres sized with 1 wt% APS

| Ratio          | Recovered glass fibres sized with 1 wt% APS | Liu et al. [20] | Zhuang et al. [22] | Thomason [24] | Recovered glass fibres sized with 1 wt% APS and extracted using acetone |
|----------------|--------------------------------------------|-----------------|--------------------|---------------|---------------------------------------------------------------|
| C:Si           | 2.4                                        | 2.2             | 2                  | 2.6           | 1.3                                                           |
| N:Si           | 0.26                                       | 0.36            | 0.14               | 0.05          | 0.11                                                          |
| O:Si           | 2.5                                        | 2.4             | 2.6                | 2.6           | 2.9                                                           |

Note: Data presented by Liu et al., Zhuang et al. and Thomason et al. were for virgin glass fibres

3.2 AFM images of sized fibres

Figure 3a – b shows the AFM scans of the recovered glass fibres sized with 1 wt% APS and extracted using acetone. Table 4 shows the surface roughness of the recovered glass fibres. From the AFM, more prominent than expected features were seen and this attributed to the presence of impurities. These impurities might be the undissolved polymer resin or other possible contamination associated with the virgin glass fibres. Smooth topography coupled with irregularly placed small droplets – like structure
was evident when the recovered glass fibres were coated with 1 wt% APS. The presence of this droplet-like structure on the surface was due to the hydrolysed molecules [20]. Similar smooth topography with irregularly small droplets was also observed by other researchers [22][25]. In his research, Turrion et al. [26] noted that the hydrolysed silanes are inherent in the formation of the smooth and homogeneous surface on the fibres. As the fibres were subjected to extraction process using acetone, a considerable amount of the sizing layer was peeled off thus exposing the rugged surface of the glass fibre (Figure 3b).

![AFM images](image)

**Figure 3.** AFM images (isotropic xyz scale) of the recovered glass fibres coated with 1 wt% APS before and after acetone extraction. (a) 1 wt% APS recovered glass fibre, (b) 1 wt% APS after acetone extraction. The encircled regions represent impurities on the surface.

We assumed that the sizing on the surface of the recovered glass was a thin layer and consisted of the significant amount of non-crosslinked physisorbed APS sizing, weakly chemisorbed compounds and, in part, strong chemisorbed compounds. The acetone might have removed this thin layer thus leaving the rugged surface of the recovered fibre with minimal sizing [20].

| Surface roughness | Recovered glass fibres sized with 1 wt% APS | Liu et al. [20] | Zhuang et al. [22] | Recovered glass fibres sized with 1 wt% APS and extracted using acetone |
|-------------------|---------------------------------------------|-----------------|-------------------|---------------------------------------------------------------|
| Ra, nm            | 13.4 ± 3.6                                  | < 6.4           | *17.7 ± 13.8      | 9.3 ± 4.8                                                     |

Note:
- Sign * indicates the maximum surface roughness of the fibres
- Data presented by Liu et al., Zhuang et al. and Thomason et al. were for virgin glass fibres

Fibre sizing was inherent in the increase in the surface roughness of the fibre. Thus when Zhuang et al. [22] conducted a two-stage sizing procedure, the surface roughness significantly increased as shown in...
Table 4. The values were higher than those presented by Liu et al. [20], and the values obtained from our experimental study. When the recovered fibres were immersed in acetone, the surface roughness decreased. Liu et al. [20] attributed to the removal of the physisorbed compounds present on the surface of the fibres. Significant extraction of the compounds mentioned above exposed the strong chemisorbed compounds to acetone thereby leading to further extraction and reduction in the surface roughness.

4. Conclusion
Experimental studies on the effect of chemical recycling with ultrasound cavitation process on the interfacial properties of the recovered fibres was investigated. Recovered glass fibres were sized with 1 wt% APS coating and analysed using XPS and AFM. The results of sized glass fibres recovered from the chemical recycling process differed with those of virgin glass fibres and this was attributed to the decrease in the quality of the recovered fibres due to the chemical recycling method used and the presence of impurities. AFM images showed the different topographies of sized glass fibres before and after extraction using acetone. From the AFM images, the APS sizing created a smoother surface and increased the surface roughness impurities and that the surface roughness decreased after immersing the samples in acetone. The decrease in quality and presence of impurities raises unanswered questions. Since this is an ongoing research, future research will focus on developing a treatment process that would increase the quality of the recovered glass fibres as well as reduce the impurities present in the glass fibres.

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6. References
[1] Rosato D V, Rosato D V, Murphy J 2005 Reinforced plastics handbook (New York: Elsevier) p 1082.
[2] Thomason J, Jenkins P, Yang L 2016 Fibers 4 18. Doi: 10.3390/fib4020018
[3] Karidis A Fiberglass demand could open up glass recycling market. Waste 360. http://waste360.com/glass/fiberglass-demand-could-open-glass-recycling-market?NL=WST-08&Issue=WST-08_20160721_WST-08_231&sftve4enews=42%cL=article_1_b&utm_rid=CPEQW000005143809&utm_campaign=7919&utm_medium=email&elq2=e72c9c0e71bd4f3e946ea3571cd31ac. [Accessed on 23 July 2016].
[4] Yang Y, Boom R, Irion B, van Heerden D-J, Kuiper P, de Wit H 2012 Chem. Eng. Process. Process Intensif. 51 53. Doi: 10.1016/j.cep.2011.09.007
[5] Hedlund-åström A 2005 Model for End of Life Treatment of Polymer Composite Materials (Stokholm: Royal Institute of Technology) p 165
[6] Ribeiro M, Fiúza A, Ferreira A, Dinis M, Meira Castro A, Meixedo J, Alvim M 2016 Recycling 1 178. Doi: 10.3390/recycling1010178
[7] Lee S H, Yoon K Y 2013 J. Korean Soc. Mar. Environ. Energy 16, 53. Doi: 10.7846/JKOSME.2013.16.1.53
[8] Feng Y C, Zhao F Q 2016 IOP conference series: Materials Science and Engineering Vol 167 012056. Doi: 10.1088/1757-899X/167/1/012056
[9] Kinoshita H, Kaizu K, Hasegawa S, Ando T, Kawamura R, Ikeda K, Kobayashi T, Fukuyama H 2013 Journal of Environment and Engineering 8 27–40, 2013.
[10] Okajima I, Watanabe K, Sako T Journal of Advanced Research in Physics 3, 1–4, 2012.
[11] Nakagawa M, Kasuga K, Aoyagi K, Ishihara K, Ikeda Y 2014 Proc. Amer. Soc. Ceramics Vol 56
[12] Yan H, Lu C, Jing D, Hou X 2014 *Chinese J. Polym. Sci.* **32**, 1550. Doi: 10.1007/s10118-014-1519-5

[13] Okajima I, Sako T 2015 *J. Mater. Cycles Waste Manag.* **19**, 16. Doi: 10.1007/s10163-015-0412-9

[14] Onwudili J A, Yildirir E, Williams P T 2013 *Waste and Biomass Valorization* **4**, 87. Doi: 10.1007/s12649-013-9204-4

[15] Zhao C, Shitian M, Ma W, Qian X, Zhang J, Chen X 2014 PCT Patent № WO/2014/179939.

[16] Liu T, Zhang M, Guo X, Liu C, Liu T, Xin J, Zhang 2017 *J Polym. Degrad. Stab.* **139**, 20. Doi: 10.1016/j.polymdegradstab.2017.03.017

[17] Thomason J L, Jones F R 1999 *Compos. Part A Appl. Sci. Manuf.* **30**, 1401, 1999.

[18] Wijewardane S 2015 The role of CNT and CNT/composites for the development of clean energy *Handbook of polymer nanocomposites: processing, performance and application. Volume B: Carbon nanotube based polymer composites* ed A K Mohanty, J K Pandey and K R Reddy (Berlin: Springer) pp. 543–576.

[19] Riviere J C, Myhra S 2009 *Handbook of surface and interface analysis methods for problem-solving* (Boca Raton: CRC Press) p 651

[20] Liu X, Thomason J L, Jones F R 2008 *J. Adhesion* **84**, 322, 2008. Doi: 10.1080/00218460802004386

[21] Nørgaard H, Nørgaard Petersen H, Kusano Y, Brøndsted P, Almdal K 2013 Proc. *Riso International Symposium on Materials Science (Riso)* vol 34 p. 333–340.

[22] Zhuang R C, Burghardt T, Plonka R, Liu J W, Mader E 2010 *Expres Polym. Lett.* **4**, 798. Doi: 10.3144/expresspolymlett.2010.96

[23] Thomason J L 1995 *Composites* **26**, 487. Doi: 10.1016/0010-4361(95)96806-H

[24] Thomason J L, Dwight D W 2000 *J. Adhes. Sci. Technol.* **14**, 745. Doi: 10.1163/156856100742852

[25] El Achari A, Ghenaime A, Wolff V, Caze C, Carlier E 1996 *Text. Res. J.* **66**, 483. Doi: 10.1177/004051759606600801

[26] Turrión SG, Olmos D, González-Benito J 2005 *Polym. Test.* **24**, 301. Doi: 10.1016/j.polymertesting.2004.11.006