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**OPTIMISATION OF ACID DIGESTION CONDITIONS FOR VOLUME
FRACTION MEASUREMENTS OF HARD TO DIGEST FIBRE-
REINFORCED POLYMER COMPOSITES**

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Optimisation of Acid Digestion Conditions for Volume Fraction Measurements of Hard to Digest Fibre-Reinforced Polymer Composites

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ABSTRACT

Acid digestion is a widely used method for determining matrix, fibre and void content of fibre-reinforced polymer composites. Current test standards governing the use of these methods prescribe, for some polymer systems, particularly hazardous chemicals including sulphuric acid and hydrogen peroxide. To reduce the health and safety risks associated with the measurement, it would be beneficial for users of these standards to conduct digestion using nitric acid only, being a far safer chemical to use. In order to develop and validate methods however, there is a requirement to assess if digestion conditions are only digesting the required material, e.g. polymer matrix and not the reinforcing fibre. This Measurement Note reports on methods developed to perform digestion measurements on composite systems incorporating phenolic, cyanate ester and polyfurfuryl alcohol polymer matrices using nitric acid only. These materials were chosen as systems known to be particularly difficult to digest without attacking the fibres. The methods have been validated by characterising the appearance of residual fibres from the digestion process using scanning electron microscopy (SEM). For all polymer systems investigated in this work it was found that digestion in a mixture of 5 ml nitric acid and 5 ml deionised water for 60 mins at 160°C successfully digested the material without leaving undigested polymer or attacking the fibres. These digestion conditions include acid profiles, times and temperatures currently outside the recommendations of ISO and ASTM test standards.

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Approved on behalf of NPLML by
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1 INTRODUCTION

Fibre volume fraction and void content of fibre-reinforced polymer composites are important characteristics influencing material performance and extensively used in material analysis, as input properties for modelling alongside manufacturing quality control [1, 2]. The acid digestion method, standardised in ISO 14127:2008 [3] and ASTM D3171-15 [4], is one of the techniques most widely used by industry to measure volume fraction properties of carbon fibre-reinforced polymers (CFRP). The method involves removing the polymer matrix phase of a composite specimen through digestion in acid to leave the reinforcing fibres only. Fibre volume fraction and void content are calculated using the constituent polymer and fibre densities, the initial mass and density of the composite specimen and the mass of the fibres following matrix removal.

A number of safety precautions require consideration when carrying out the technique. For composites incorporating common epoxy matrices, the method can be conducted in a reasonably safe manner as polymer digestion is possible using concentrated nitric acid which has relatively easy to follow control measures. Different polymer types however (e.g. phenolic and cyanate ester) typically require more hazardous reagents to achieve full matrix digestion with current standards recommending mixtures including sulphuric acid and hydrogen peroxide. Due to the health and safety risks associated with the use, storage and disposal of these mixtures there is a desire to achieve digestion of these polymer types with nitric acid only. Whilst this approach reduces health and safety risks, omitting such reagents can inhibit the digestion process, putting more emphasis on developing optimum digestion conditions for a given material type. This is particularly important considering the method's assumption that the polymer matrix is fully digested by the acid without attacking and removing material from the reinforcing fibre. Regions of undigested polymer or removed fibre from acid attack will introduce errors in the measurement with the potential to over- or under-estimate fibre volume fraction and void content.

Currently there is little guidance available on how to validate that digestion conditions are appropriately digesting the composite. This Measurement Note reports on work carried out to develop and validate digestion conditions using nitric acid only for polymers where this is not currently specified in existing standards. In particular, the use of scanning electron microscopy (SEM) is employed to assess the visual characteristics of residual fibres following digestion to validate conditions have not attacked the reinforcing fibres or left regions of undigested polymer.

2 EXPERIMENTAL

2.1 MATERIALS AND SPECIMEN PREPARATION

This work has investigated acid digestion of CFRP systems incorporating phenolic, cyanate ester and polyfurfuryl alcohol polymer matrices. These have been chosen due to previous difficulty encountered when attempting to fully digest the polymer matrix without attacking the reinforcing fibre using nitric acid only. Details of the materials including cured polymer density and fibre density were provided by the material suppliers and are given in Table 1. Density values were taken from technical data sheets due to measured values of the actual constituent densities not being possible. Due to confidentiality agreements, manufacturing processing conditions have been withheld. Specimens for digestion (~1 g) were machined from supplied material using a CompCut 500 composite plate saw and dried to constant mass at 105°C before testing. Due to particular difficulty in digesting cyanate ester, specimens had to be reduced to ~0.5 g.

Table 1 – CFRP systems investigated in this work.

Composite System	Polymer Matrix	Polymer Density (g/cm ³)	Fibre Density (g/cm ³)
Solvay TM80S-NS (pre-preg)	Phenolic	1.26	1.76
Cytec MTM 110 (polymer) Tenax HTA40 E13 (fibre)	Cyanate ester	1.28	1.76
Evopreg PFC502-C650T (pre-preg)	Polyfurfuryl alcohol	1.20	1.80

2.2 VOLUME FRACTION BY MICROWAVE ASSISTED ACID DIGESTION

Acid digestion was undertaken in general accordance with the procedures described in ISO 14127:2008, Method A, Procedure 2 [3] and ASTM D3171-15, Procedure F [4]. Before digestion, the initial mass and density of each specimen was determined in accordance with the immersion method described in ISO 1183-1:2019, Method A [5]. Digestion was carried out using 70% concentrated nitric acid (HNO₃) in an Ethos Up Milestone microwave digester supplied by Analytix Ltd (Baldon, UK). Specimens were placed inside vessels with the chosen acid profile (acid type, quantity and mixing ratio) and ramped to reach the set digestion temperature within 10 mins. Temperature was maintained to $\pm 2^\circ\text{C}$ by automatic adjustment of the microwave output power which was limited to a maximum of 800 W. Following digestion the contents of the vessel were cooled to $\sim 65^\circ\text{C}$ and the reinforcing fibres separated from the acid solution using a vacuum pump to pull the acid and digestion residue through a pre-weighed filter. The residual fibres were washed several times through the filter using deionised water and acetone before being dried to constant mass at 105°C . All mass measurements were made to 0.1 mg using a calibrated Mettler Toledo X105 analytical balance. The fibre volume fraction (V_f) was subsequently calculated using the mass of the fibres following digestion (M_f), the mass of the initial specimen (M_i), constituent fibre density (ρ_f) and the density of the composite (ρ_c):

$$V_f = \frac{M_f}{M_i} \frac{\rho_c}{\rho_f} [\times 100] \quad (1)$$

Digestion parameters including acid profile, digestion time and temperature were varied during the course of experiments to achieve successful matrix removal. Once an optimised set of digestion parameters had been established, (see Section 2.3) five repeats at those conditions were carried out to assess repeatability.

2.3 SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) was used to validate digestion parameters by visually assessing the condition of residual fibres and checking for either fibre attack or regions of undigested polymer. SEM images were taken using either the InLens or SE2 detector in a Zeiss Supra SEM at an accelerating voltage of 2.5 or 5.0 kV and a 20 μm aperture.

3 RESULTS AND DISCUSSION

3.1 DIGESTION USING CONCENTRATED NITRIC ACID (70% HNO₃)

Initial digestion runs evaluated typical conditions when digesting with nitric acid (HNO₃) as recommended in ISO 14127:2008 [3] and ASTM D3171-15 [4]. Specimens were digested in 20 ml of 70% concentrated HNO₃ for 30 mins at temperatures between 120 and 160°C. Previous studies [6] had shown temperature to be the dominant factor influencing digestion, so was initially chosen as the main variable.

Figure 1 shows SEM micrographs taken of the residual fibres from digesting phenolic composite specimens in 70% concentrated HNO₃ for 30 mins at 120 and 160°C. At these two ends of the temperature range, evidence of both undigested polymer and fibre attack were observed. Whilst the bulk of the polymer resin has been removed at 120°C (Figure 1(a)), a ‘stained like’ appearance was noted on the surface of some of the fibres indicating fibre attack. At the higher digestion temperature of 160°C (Figure 1(b)) further indication of fibre attack is present, observed as a flaky appearance of the fibre surface where material has been removed by the acid. Even at these higher temperatures this micrograph also shows regions of undigested polymer present amongst the fibres. These regions show up as high contrast areas that result from the ‘charging’ of the polymer that occurs in the SEM due to the non-conductive nature of the polymer [7]. These results show that using the recommended acid profile (20 ml of 70% HNO₃), no temperature window exists in which the material can be optimally digested. Similar observations were seen when analysing cyanate ester and polyfurfuryl alcohol under these conditions.

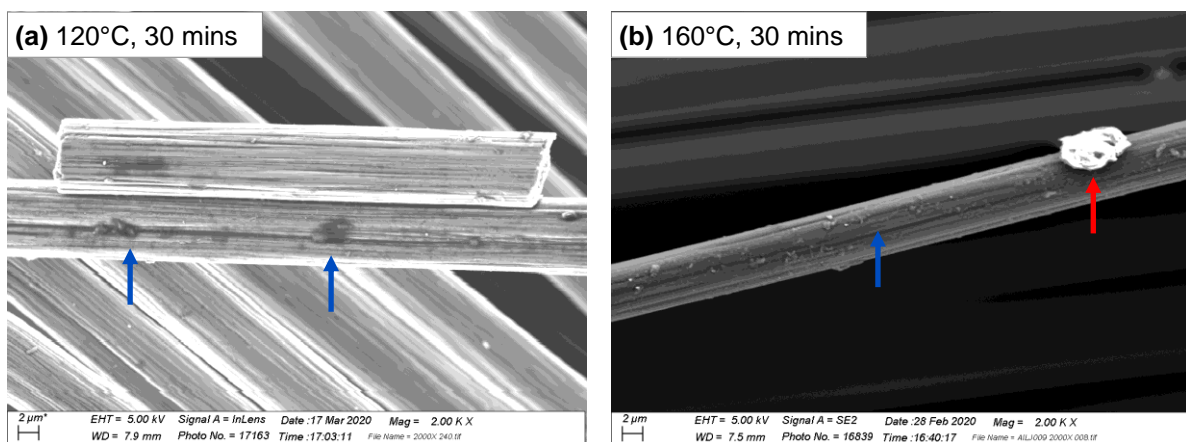


Figure 1 – SEM micrographs of the residual fibres from digestion of phenolic composite after 30 mins using 70% concentrated HNO₃ at (a) 120°C, and (b) 160°C. Blue and red arrows indicating attacked fibre and undigested polymer, respectively.

3.2 DIGESTION USING DILUTED NITRIC ACID (35% HNO₃)

The results using 70% concentrated HNO₃ indicated digestion conditions were too aggressive and a more controlled treatment of the specimen was required to remove the polymer matrix without attacking the fibres. To achieve better control, digestions were undertaken by diluting 70% HNO₃ in deionised water at a 1:1 ratio, effectively reducing the acid concentration to 35%. Specimens of all material types were digested in a mixture of 5 ml HNO₃ and 5 ml deionised water over a range of time and temperatures and the residual fibres assessed under SEM.

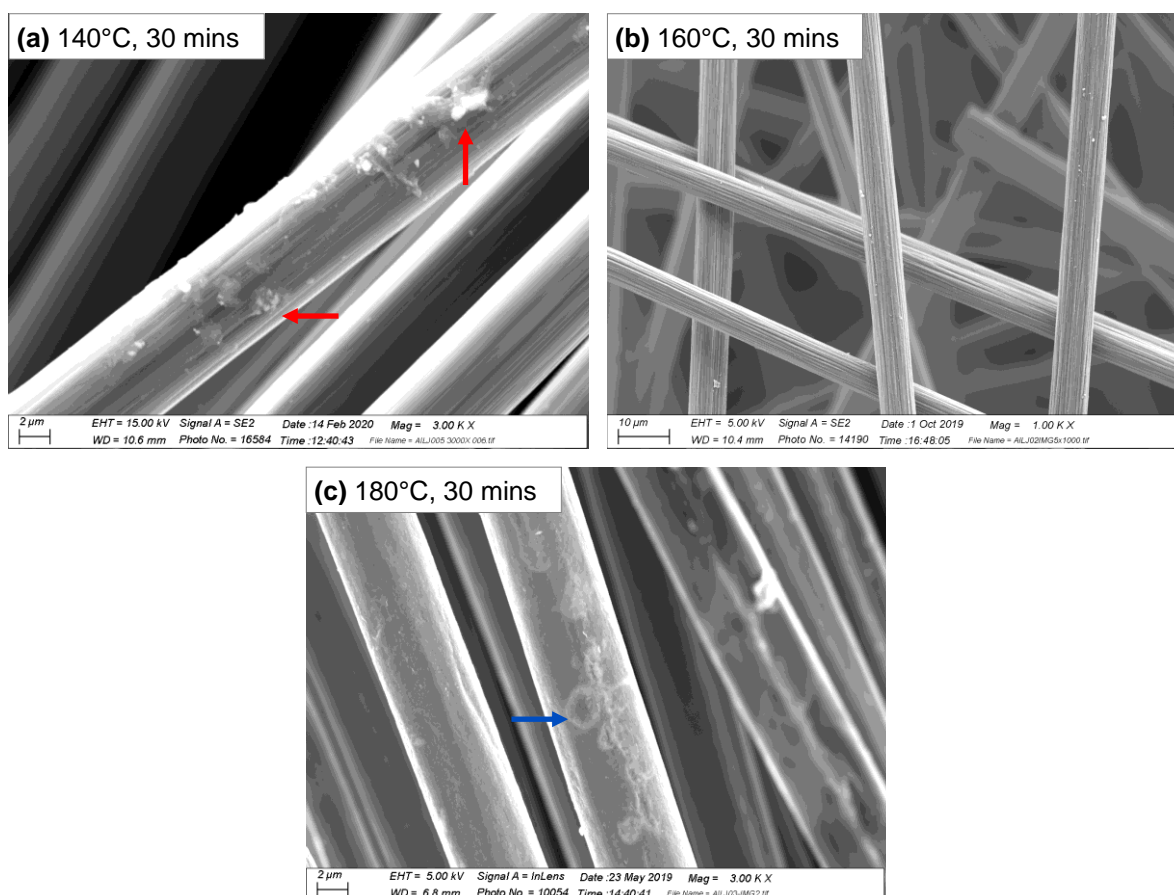


Figure 2 – SEM micrographs of the residual fibres from digesting phenolic composite for 30 mins using 35% concentrated HNO₃ at (a) 140°C, (b) 160°C, and (c) 180°C. Blue and red arrows indicating attacked fibre and undigested polymer, respectively.

SEM micrographs of the residual fibres following digestion for 30 mins using 35% HNO₃ for composite systems containing phenolic, polyfurfuryl alcohol and cyanate ester are shown in Figures 2, 3 and 4, respectively. Figure 2 shows the evolution of residual fibre condition with changing digestion temperature for the phenolic composite. At 140°C regions of undigested polymer can be observed on the fibre surface (Figure 2(a)). As the temperature was increased to 160°C the acid has removed all of the polymer phase without affecting the fibre condition (Figure 2(b)). Some very fine debris is observed and whilst it is unknown if this is undigested polymer or other constituents such as a filler, it is assumed these will have little effect on calculated values of fibre volume fraction. On increasing digestion temperature further to 180°C, evidence of acid starting to attack the fibre is observed from the stained appearance on the fibre surface. In addition, the striations that can be observed on the clean fibres at 160°C are not present, further indicating removal of fibre material. Similar observations were seen for polyfurfuryl alcohol, although complete removal of the polymer matrix was possible at lower temperatures. Only at 100°C (Figure 3(a)) were some small regions of undigested polymer seen.

In contrast, cyanate ester specimens presented greater difficulty in achieving complete polymer digestion without fibre attack despite reducing the specimen size from 1.0 to 0.5 g. Figure 4(a) shows the residual fibres after digestion at 160°C and whilst these appear clean, large macroscopic clumps of undigested polymer were present in the filter from the filtration process following digestion. As with phenolic and polyfurfuryl alcohol specimens, increasing digestion temperature above 160°C showed evidence of fibre attack (Figure 4(b)). To achieve complete matrix removal for cyanate ester specimens,

further trials were carried out increasing the digestion time to 60 mins. Complete digestion with no observations of undigested polymer was found to be possible at 160°C as evidenced in Figure 5(b).

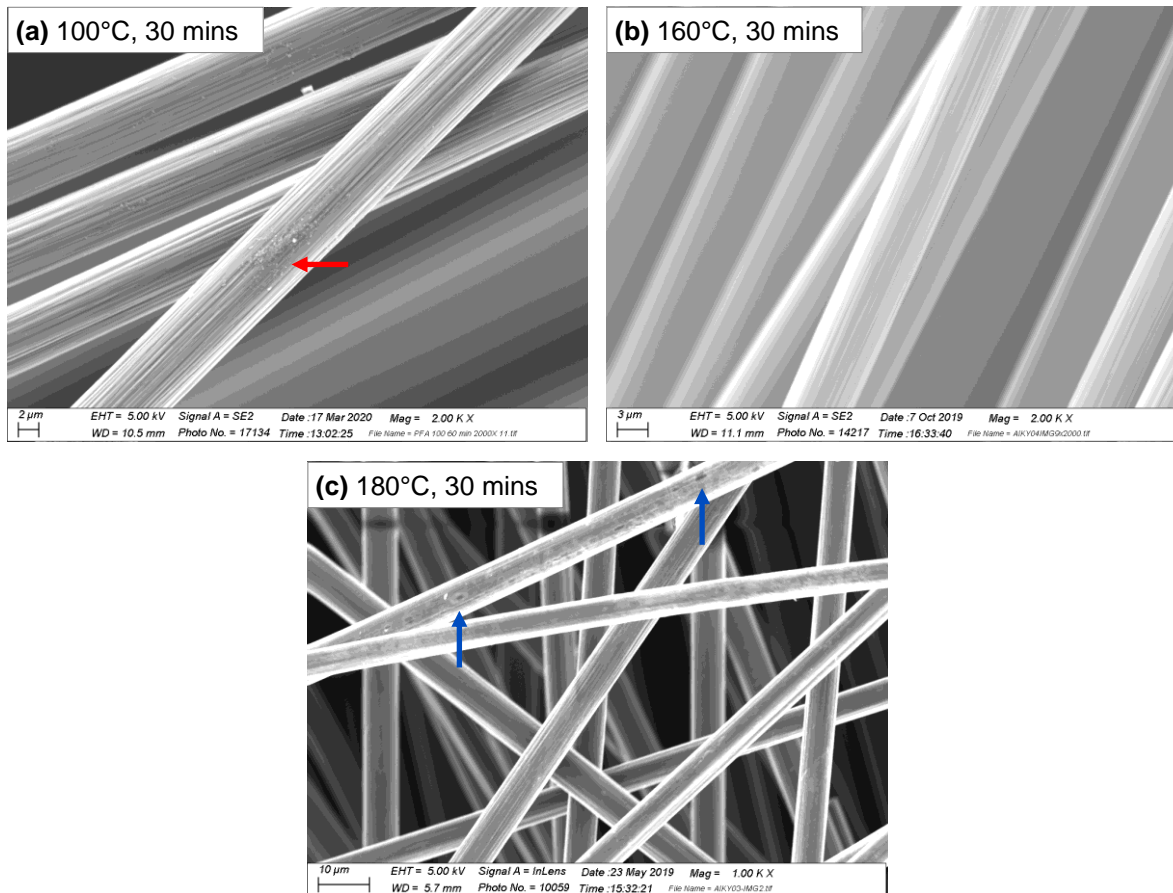


Figure 3 – SEM micrographs of the residual fibres from digesting polyfurfuryl alcohol composite for 30 mins using 35% concentrated HNO_3 at (a) 100°C, (b) 160°C, and (c) 180°C. Blue and red arrows indicating attacked fibre and undigested polymer respectively.

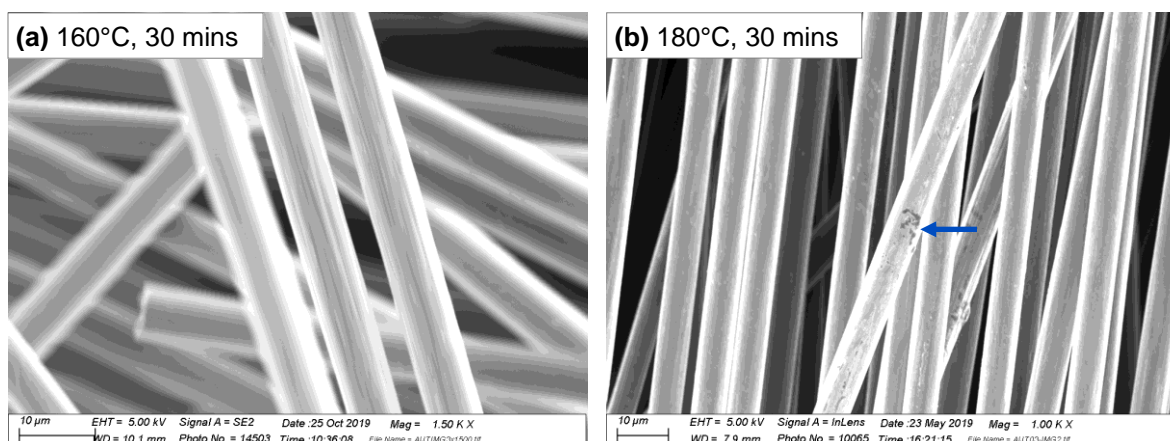


Figure 4 – SEM micrographs of the residual fibres from digesting cyanate ester composite for 30 mins using 35% concentrated HNO_3 at (a) 160°C, and (b) 180°C. Blue and red arrows indicating attacked fibre and undigested polymer respectively.

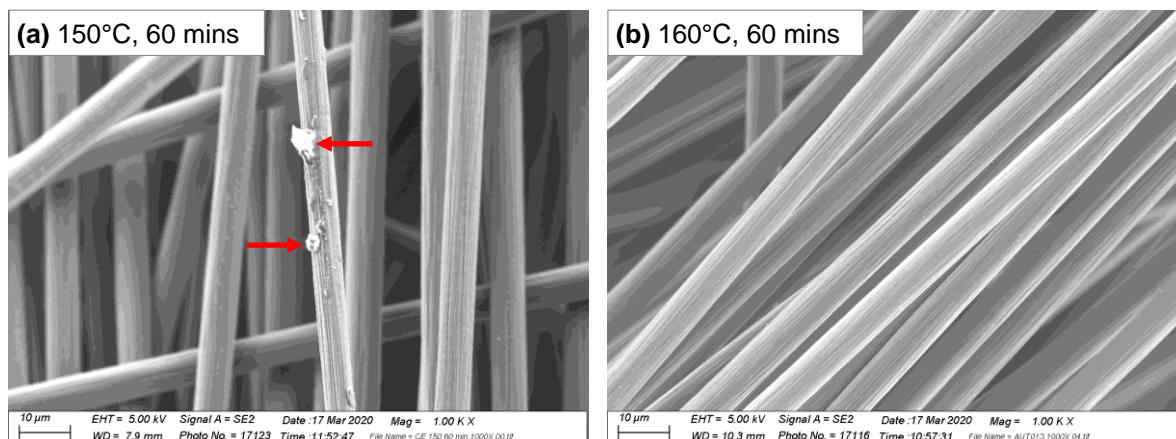


Figure 5 – SEM micrographs of the residual fibres from digesting cyanate ester composite for 60 mins using 35% concentrated HNO_3 at (a) 150°C, and (b) 160°C. Red arrows indicating undigested polymer.

Digestions at 160°C for 60 mins were also carried out for the phenolic and polyfurfuryl alcohol materials to assess the influence of extended digestion time on these materials. Figures 6 shows micrographs for the residual fibres following digestion for all materials at 160°C for 60 mins. These show that increasing digestion time at 160°C does not appear to further initiate fibre attack. Interestingly, although the different materials investigated use different grades of carbon fibre, the evidence from all SEM micrographs indicate fibre attack is only initiated with this acid profile at digestion temperatures above 160°C.

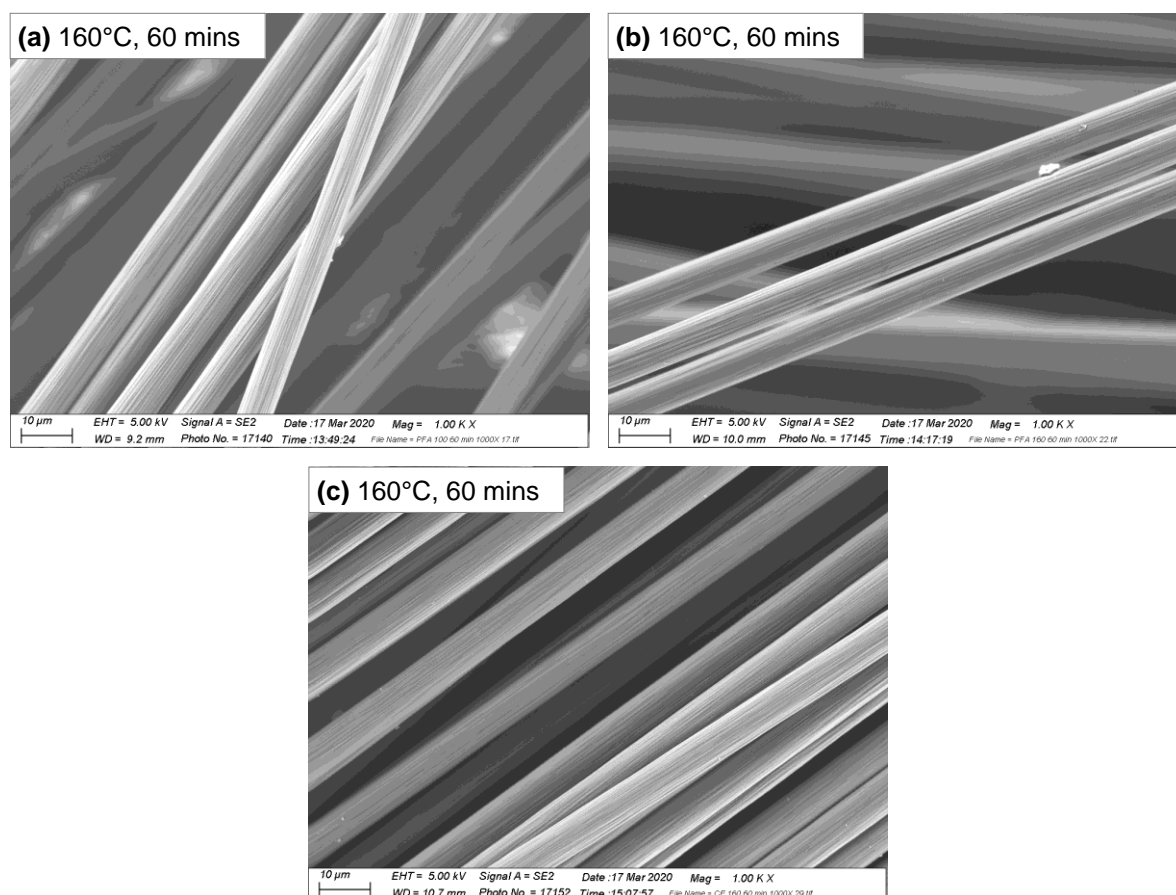


Figure 6 – SEM micrographs of the residual fibres from digesting (a) phenolic, (b) polyfurfuryl alcohol, and (c) cyanate ester composites for 60 mins using 35% concentrated HNO_3 at 160°C.

The analysis of residual fibres with SEM has indicated that polymer digestion with nitric acid only is possible for composites comprising of a range of different matrices as well as epoxy. The digestion conditions shown to be successful are currently outside those recommended in ISO 14127:2008 [3] and ASTM D3171-15 [4]. It is suspected that this has been achieved by creating a more controlled digestion of the material. By reducing the HNO_3 concentration the polarity of the acid mixture is lowered enabling slower microwave absorption during heating. This, combined with the weaker acid reducing pressure inside the reaction vessel, would result in a more controlled, less aggressive digestion process, enabling the polymer to become fully digested without fibre attack.

3.3 FIBRE VOLUME FRACTION MEASUREMENTS

In order to further validate digestion conditions, five repeat digestions at 160°C for 60 mins were carried out on all materials. The results for calculated fibre volume fraction (V_f) are given in Tables 2, 3 and 4. Values for void content (V_v) have not been reported due to the high uncertainty of the theoretical values for polymer density used to calculate V_v leading to erroneous values. Had more accurate polymer density values been measured or known, V_v could have been easily derived. The high level of repeatability observed from the low coefficients of variation (CV) further indicate optimal digestion. Large variability would be expected if either under- or over-digestion was present. The higher CV for cyanate ester specimens is likely a result of these specimens being of smaller volume (0.5 g) and therefore individual specimens potentially encompassing different sections of the unit cell of the composite.

Table 2 – Density (ρ_c) and fibre volume fraction (V_f) for phenolic specimens.

Specimen	Density, ρ_c (g/cm ³)	Fibre Vol. Fraction, V_f (%)
Phenolic - 1	1.504	55.2
Phenolic - 2	1.507	57.2
Phenolic - 3	1.509	56.3
Phenolic - 4	1.508	56.7
Phenolic - 5	1.506	56.9
Mean	1.507	56.4
Standard deviation	0.002	0.8
CV (%)	0.12	1.38

Table 3 – Density (ρ_c) and fibre volume fraction (V_f) for polyfurfuryl alcohol specimens.

Specimen	Density, ρ_c (g/cm ³)	Fibre Vol. Fraction, V_f (%)
Polyfurfuryl alcohol - 1	1.578	56.0
Polyfurfuryl alcohol - 2	1.570	54.8
Polyfurfuryl alcohol - 3	1.571	54.7
Polyfurfuryl alcohol - 4	1.579	56.3
Polyfurfuryl alcohol - 5	1.571	55.1
Mean	1.574	55.4
Standard deviation	0.004	0.7
CV (%)	0.28	1.28

Table 4 – Density (ρ_c) and fibre volume fraction (V_f) for cyanate ester specimens.

Specimen	Density, ρ_c (g/cm³)	Fibre Vol. Fraction, V_f (%)
Cyanate ester - 1	1.518	55.5
Cyanate ester - 2	1.526	56.5
Cyanate ester - 3	1.491	52.3
Cyanate ester - 4	1.493	55.3
Cyanate ester - 5	1.487	52.6
Mean	1.503	54.4
Standard deviation	0.018	1.9
CV (%)	1.18	3.46

4 CONCLUSIONS AND FURTHER WORK

This work has established methods for carrying out acid digestion using nitric acid only on materials where this is not currently stipulated in standards. By omitting the use of hazardous reagents such as hydrogen peroxide and sulphuric acid, the developed methods significantly reduce the health and safety risks associated with this measurement. Further, the digestion conditions established have included temperatures and times outside of those currently recommended within ISO 14127:2008 [3] and ASTM D3171-15 [4]. Validation of digestion conditions was conducted through characterising the appearance of undigested polymer and attacked fibres in the residual material from digestion. These visual characteristics are of use for validating digestion conditions on other materials and where alternative digestion systems are used.

An interlaboratory study including other polymer types in which hazardous reagents are recommended would further confirm the methodologies outlined within this measurement note. Such an investigation could also establish the reproducibility and repeatability of the method required for standardisation.

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