

The fibre fraction of fibre reinforced polymer composites strongly influences the properties and performance of the materials. Its determination in polymer composites is analytically challenging due to the difficulty in designing an efficient and selective protocol for separating the polymer matrix of composite samples without affecting the fibres. Microwave sample preparation has been successfully applied due to its selectivity and efficiency achieved by selective acid digestion. This study, carried out by the National Physical Laboratory in the UK, describes a unique and innovative microwave protocol to selectively digest only the polymer matrix without affecting the reinforcing fibres or leaving regions of undigested polymer, followed by visual characterisation of the residual fibres using scanning electron microscopy (SEM).

INTRODUCTION

Fibre volume fraction and void content of fibre-reinforced polymer composites are important properties that influence material performance and are therefore widely used in material analysis^{1,2}. The acid digestion method, standardised in ISO 14127:2008³ and ASTM D3171-15⁴ procedures, is one of the most widely used techniques by industry to measure volume fraction properties of carbon fibre reinforced polymers (CFRP). The method involves removing the polymer matrix phase of a composite sample through digestion in acid to leave the reinforcing fibres only. Fibre volume fraction and void content are then calculated considering the constituent polymer and fibre densities, the initial mass and density of the composite sample and the mass of the fibres following matrix removal. For common epoxy matrices containing composites, the method can be carried out safely as polymer

digestion can be performed with concentrated nitric acid. However, other polymer types (e.g. phenolic and cyanate esters) typically require more hazardous reagents to achieve complete matrix digestion, including sulphuric acid and hydrogen peroxide mixtures.

A milder chemical approach using nitric acid alone is desirable, allowing analysts to reduce the number of chemicals used and the associated risks. Although this approach reduces health and safety risks, the omission of such reagents can affect the digestion process, requiring optimisation of the digestion conditions for a particular type of material. This is particularly important as the method assumes that the polymer matrix is completely digested by the acid without attacking and removing material from the reinforcing fibre.

APPLICATION REPORT

Fibre fraction determination in polymer composites



Microwave sample preparation has been successfully and widely applied for both elemental and molecular analysis thanks to its efficiency and selectivity achievable with volumetric heating. In this application report, a selective microwave assisted sample preparation protocol has been developed by National Physical Laboratory (NPL) for the volume fraction determination of fibre-reinforced polymer composites. The innovative microwave protocol ensures a selective digestion of polymer matrix without attacking the reinforcing fibre or left regions of undigested polymer. The protocol was performed with ETHOS UP with the aim to develop a fast and easy-to-apply protocol for routine high throughput analysis, based on nitric acid only.

EXPERIMENTAL

EQUIPMENT

- Milestone's ETHOS UP
- SK-15 (TFM 100 mL vessels)
- CompCut 500 composite plate saw
- Drying oven
- Analytical balance
- Scanning Electron Microscopes (SEM)



Figure 1. Milestone's ETHOS UP with SK 15 rotor

MATERIAL AND REAGENTS

For the filtration process, a filter paper was pre-weighed. After the filtration, the filter was washed several times with deionized water and acetone before being dried at constant mass at 105°C in an electric oven.

SAMPLES

To evaluate the polymer composites degradation when submitted to acid digestion, hard to digest CFRP were used such as phenolic, cyanate ester and polyfurfuryl alcohol polymer.

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

Table 1 – CFRP system tested.

Samples for digestion, approximately 1 g, were machined from supplied material using a CompCut 500 composite plate saw and dried to constant mass at 105°C before testing. For cyanate ester approximately 0.5g of sample was used due to the sample type.

SAMPLE PREPARATION

In this study, 0.5-1 g of fibre-reinforced polymer composites samples have been treated with a mixture of 5 mL of 70% HNO₃ and 5 mL of deionised water over a range of time and temperatures. Diluted acid (35%) obtained by diluting 70% HNO₃ in deionised water at a 1:1 ratio allows to better control the digestion process of the polymeric part.

Before digestion, the initial mass and density of each sample was determined in accordance with the immersion method described in ISO 1183-1:2019 (method A)⁵. The sample and acid mixture were placed directly into the TFM digestion vessel and then the system was properly sealed with a PTFE cap and a spring to ensure hermetically closure during the run.

In order to evaluate the efficiency of the polymer matrices digestion, the residual fibres were determined by SEM.

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MICROWAVE PROCESS AND QUANTIFICATION

The MW program used for this work was the following:

Step	Time (min)	Power (W)	T(°C)
1	10	800	160
2	60	800	160

Table 2 - Microwave Program

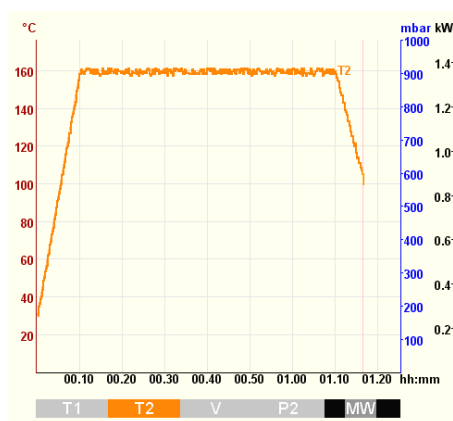


Figure 1 – Microwave run profile

After the microwave program, the digestates were cooled to ~65°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 with deionised water and acetone before being dried to constant mass at 105°C in an oven.

ANALYTICAL STEP

The fibre volume fraction (V_f) was subsequently calculated according to the following equation:

$$V_f = \frac{M_f \times \rho_c}{M_i \times \rho_f} \times 100$$

Where:

M_f is the mass of the fibres after digestion

M_i is the initial mass of the sample

ρ_f is the constituent fiber density

ρ_c is the composite density

RESULTS AND DISCUSSION

The microwave sample preparation protocol on polymer composites developed in this study has been designed to determine the fibre volume fraction *via* scanning electron microscopy technique. The applicability of such protocol strongly depends on the capability of the digestion method to selectively digest the polymer matrix without degrading the reinforcing fibres.

Initial digestion runs evaluated typical conditions when digesting with HNO_3 as recommended in ISO 14127:2008 and ASTM D3171-15. Specimens were digested in 20 ml of 70% concentrated HNO_3 for 30 mins at temperatures between 120 and 160°C. These conditions were not suitable for the purpose since as reported in the SEM micrographs (Figure 2) fibres were attacked, and undigested polymer was detected.

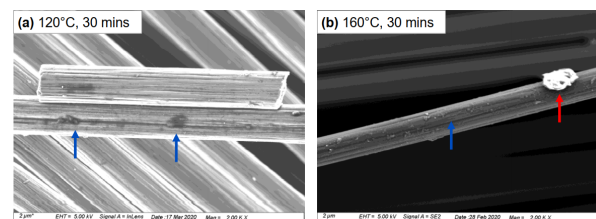
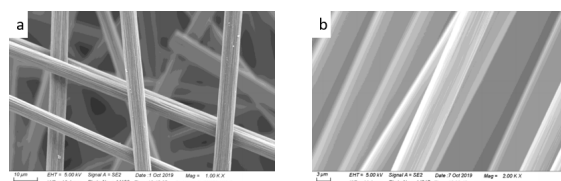


Figure 2 - SEM micrographs of the residual fibres from digestion of phenolic composite after 30 mins using 70% concentrated HNO_3 at (a) 120° C, and (b) 160° C. Blue and red arrows indicating attacked fibre and undigested polymer, respectively.

Following an in deep method optimization, the most selective condition in terms of temperature, time and acid concentration were 1:1 HNO_3 : deionized H_2O digestion mixture working at 160°C for 60 min. As reported in Figure 3, SEM micrographs shown integrity of the fibre morphology and no evidence of residual polymer.



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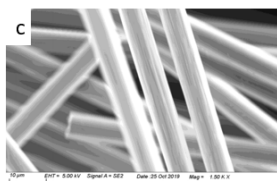


Figure 3 – SEM micrographs of the residual fibres from digesting (a) phenolic, (b) polyfurfuryl alcohol, (c) cyanate ester composites for 30 mins using 35% concentrated HNO_3 at 160°C .

Tables 3, 4 and 5 report the fibre volume fraction of different polymer matrices working under optimized conditions. 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 composites is likely a result of these samples being of smaller volume (0.5 g) and therefore individual samples potentially encompassing different sections of the unit cell of the composite.

Sample	Density ρ_c (g/cm ³)	Fibre volume 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 and fibre volume fraction results for phenolic samples

Sample	Density ρ_c (g/cm ³)	Fibre volume 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 and fibre volume fraction results for polyfurfuryl alcohol samples

Sample	Density ρ_c (g/cm ³)	Fibre volume 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

Table 5 – Density and fibre volume fraction results for cyanate ester samples

These results have 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, allowing the polymer to be fully digested without fibre attack.

Despite the described protocol is outside the ISO 14127:2008 and ASTM D3171-15 recommendations, the data reported in this study candidate the microwave method to a good complementary and alternative approach to the traditional protocol, using a much less harsh chemicals.

CONCLUSION

The determination of fibre volume fraction in polymer composites is analytically challenging due to the difficulty in designing an efficient and selective protocol to separate the polymer matrix of composite samples without affecting the reinforcing fibres. The new selective digestion protocol developed in this study using the Milestone ETHOS UP and dilute acid (1:1 70% HNO_3 : deionised H_2O) ensures complete polymer digestion while leaving the residual fibres unaffected.

The developed protocol is fast, with a duration of only 60 minutes, cost effective and allows a significant reduction in the number of reagents used in conventional protocols.

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The described method aims to be an efficient evolution of the ISO 14127:2008 and ASTM D3171-15 method in a greener chemical concept.

ACKNOWLEDGEMENTS

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