

## THERMAL AND MECHANICAL BEHAVIOUR OF PHORMIUM TENAX REINFORCED POLYPROPYLENE COMPOSITES

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### Abstract

*Composites of Phormium tenax fibres in a polypropylene matrix with fibre content up to 40 wt%, produced by injection moulding and twin screw compounding, have been characterized by scanning electron microscopy, differential scanning calorimetry, thermogravimetric analysis and mechanical test. The results have shown that the main degradation peak for polypropylene was slightly shifted to higher temperatures with increasing content of fibres, thus improving the thermal stability of the composites. The introduction of fibres did not result in a significant variation in the position of the peaks for calorimetric analysis, except for the melting peak, which appeared lower for the composites with respect to the neat matrix. A slight increase in crystallinity was also measured. Tensile modulus has been increased by reinforcing the matrix with growing amounts of fibres, whilst the effect on tensile strength was not evident.*

### 1 Introduction

The depletion of petroleum resources coupled with growing environmental regulations are stimulating the search for materials and products with the lowest environmental “footprint” possible. In this regard, biocomposites made from natural fibres and petroleum-derived non-biodegradable polymers, like polypropylene (PP), polyethylene (PE) and epoxies, can represent a suitable alternative to glass fibre reinforced composites and provide potential value-added source of income to the agricultural community [1, 2].

One major area of development over the last decade has been in the use of natural fibre reinforced thermoplastic composites. The use of thermoplastic composites offers several advantages compared to that of thermoset ones. These useful properties include high impact resistance, damage tolerance, low price and recyclable properties. Currently, the main areas of application of thermoplastic natural fibre composites are packaging, transportation and building industries. Polypropylene is perhaps the most commonly used polymer to produce thermoplastic natural fibre composites, even though other synthetic polymers, such as polyethylene, polystyrene (PS) and polyamides (PA), are also common in natural fibre composites. In addition, also natural and biodegradable polymers (such as poly(lactic acid) PLA, polycaprolactone (PCL), poly( $\beta$ -hydroxybutyrate (PHB)) are being considered as

matrices for the next generation of “green” composites. Of all thermoplastics, PP shows the most potential benefits when combined with natural fibres for making composites of industrial value [3]. Several types of natural fibres have been investigated in PP (such as flax, hemp, kenaf, jute, wood flour, abaca, sisal, date palm, coconut, pineapple, ramie, vetiver, etc.) and the resulting composites and properties have been also recently reviewed [4].

Among natural fibres, leaf fibres appear promising for obtaining long stretches of aligned fibres. In recent years, a renewed interest has been shown for fibres extracted from the leaves of the *Phormium tenax* [5, 6], commonly known as harakeke or New Zealand flax, a monocotyledonous plant which is endemic to New Zealand. Harakeke is a significant source of fibre, which has a traditional use by the Maori people as a fibre for weaving mats and ropes [7]. The use of Phormium fibres as filler in plastics has often been proposed, both in thermosets [8-11] and thermoplastics [12, 13]. Thermoset-based composites are well characterized, however very few data are available on thermoplastic reinforced composites. In order to extend the potential applications of Phormium tenax fibres, a detailed mechanical and thermal characterization of these composites is needed.

To this purpose, this experimental work is aimed at investigating the use of untreated Phormium tenax fibres as reinforcement in polypropylene matrix. Several properties were studied, including mechanical and thermal ones. The morphologies of the fractured specimens using a scanning electron microscope (SEM) were also investigated.

## 2 Materials and testing methods

Polypropylene homopolymer (Moplen HP 501-L) was supplied by Lyondell Basell. As per supplier's data, HP 501-L has the following properties: melt flow rate (MFR) is 6.0 g/10 min (230°C/2.16 kg), density is 0.9 g/cm<sup>3</sup>, tensile stress at yield is 34.0 MPa, tensile modulus is 1500 MPa, tensile strain at break exceeds 50 %. Phormium tenax fibres were collected from New Zealand. Leaves were stripped and the hanks of fibres were washed and then paddocked and scutched, according to the typical procedure followed on these fibres [12]. The fibres were cut to a length of 2-3 mm.

PP composites were manufactured using a twin-screw microextruder (DSM Explore 5&15 CC Micro Compounder) and mixing process parameters (100 rpm screw speed, 1 min mixing time and temperature profile: 170 – 180 – 190°C) were modulated in order to optimize material final properties. To obtain the desired specimens for the characterization, the molten composite samples were transferred after extrusion through a preheated cylinder to a mini injection mould ( $T_{\text{mould}} = 25^{\circ}\text{C}$ ,  $P_{\text{injection}} = 8$  bar). Composites were prepared with different amount of phormium fibres: specifically, a masterbatch containing 40 wt.% of phormium fibres was prepared (PP40PH), while the other compositions (20 wt.% and 30 wt.% (designed as PP20PH and PP30PH, respectively) were obtained diluting the master with neat PP.

Tensile tests were performed in accordance with the UNI EN ISO standard 527/2: the type IBA sample was used for tensile testing with an initial grip length of 5 mm. Loading was applied in displacement control, using a load cell of 30 kN by means of a digital Lloyd Instrument LR 30K with a crosshead speed of 5 mm/min. Average tensile strength, percentage deformation at break and elastic modulus (E) were calculated from the resulting stress-strain curves. The measurements were performed at room temperature and at least five samples were tested, expressing the results as mean value and standard deviation.

Thermogravimetric analysis was performed on 10-mg samples on a Seiko Exstar 6000 TGA quartz rod microbalance. The tests were carried out in nitrogen flow (250 ml min<sup>-1</sup>) from 30 to 900°C with a 10°C min<sup>-1</sup> heating ramp.

Differential scanning calorimeter (DSC TA Q200) measurements were performed in the temperature range from -25 to 250°C, at 10°C/min, performing two heating and one cooling scans. The peak temperatures for melting and crystallization were evaluated and the degree of crystallinity of the sample was calculated taking as reference 191.3 J/g [14] as heat of melting of the fully crystalline sample according to the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0(1 - w_{fibre})} \quad (1)$$

where  $\Delta H_m$  is the enthalpy of melting (J/g),  $\Delta H_m^0$  is the enthalpy of melting for 100% crystalline PP (J/g) and  $w_{fibre}$  is the weight fraction of Phormium fibres.

A Hitachi S-2500 scanning electron microscope was used to investigate fracture surfaces of composites. Prior to observation, the specimens were gold coated.

### 3 Results and discussion

Figure 1 and Table 1 show typical tensile curves and properties for neat PP and PP/Phormium composites, respectively. The results indicate that the tensile strength and modulus increase with increasing Phormium content. Tensile modulus has been consistently increased by reinforcing the composite with growing amounts of fibres, whilst the effect on tensile strength is less evident, as is the case in a large number of lignocellulosic fibre composites. This increment in the modulus is in agreement with findings from literature [15, 16] that adding fillers to a thermoplastic polymer restrains the movement of its chains, thereby increasing the stiffness. The addition of Phormium fibres did not largely improve the tensile strength: this is also a common trend for natural fibre reinforced composites. This behaviour is usually an indication of poor adhesion between natural fibres and polymers and, as a consequence, of not very effective stress transfer across the interface. Generally, tensile strength is much more dependent on interfacial adhesion than the Young's modulus is [16].

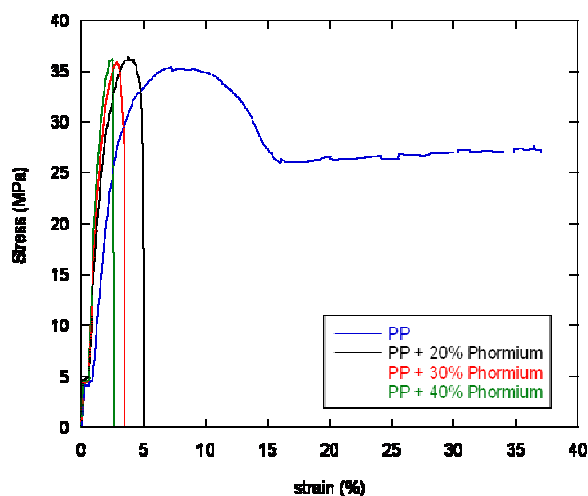
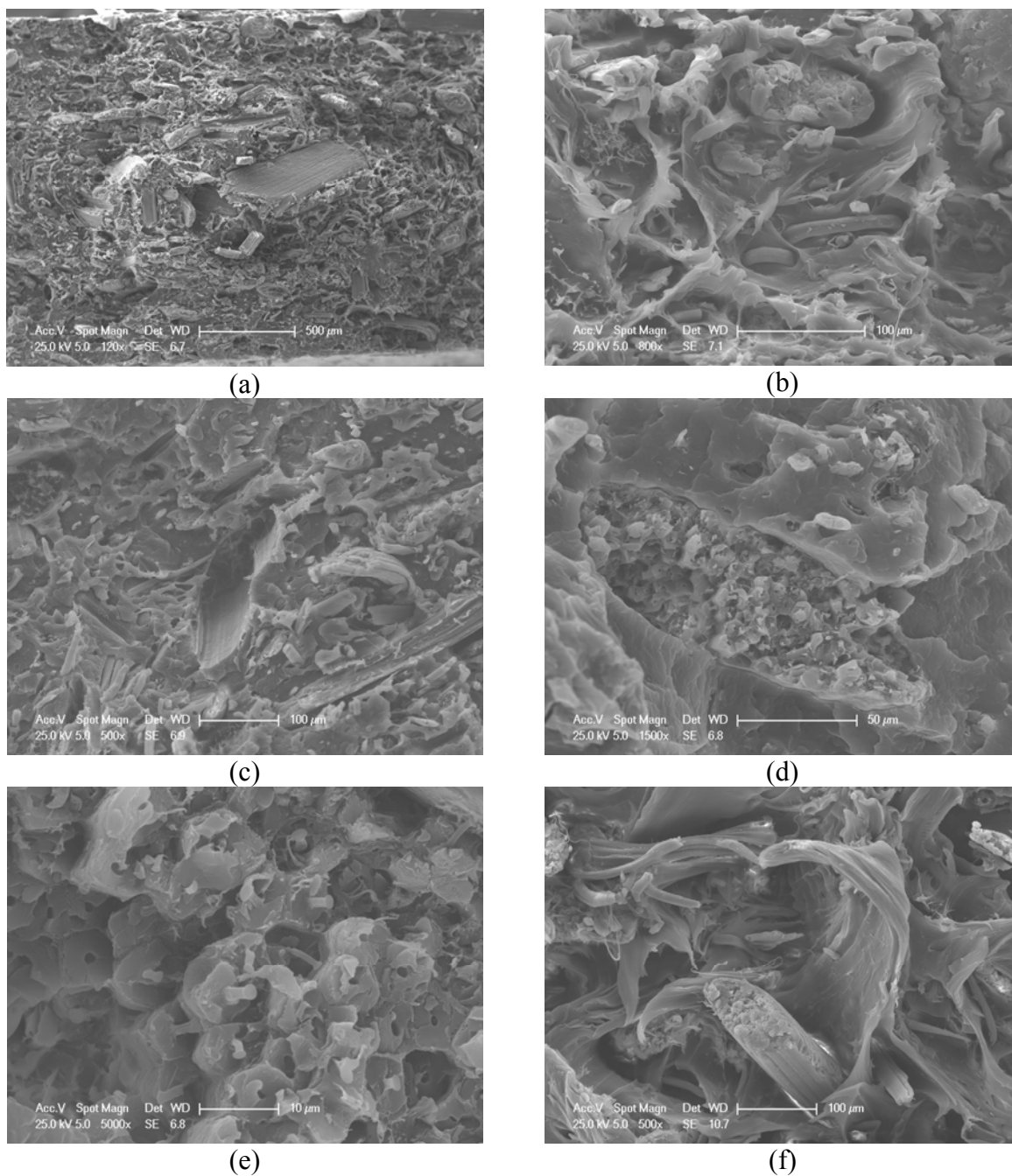


Figure 1. Typical tensile curves for neat PP and PP/Phormium composites

Materials	Tensile strength (MPa)	Young's Modulus (GPa)
PP	35.24 ± 0.26	1.94 ± 0.17
PP20PH	36.13 ± 0.50	2.94 ± 0.25
PP30PH	35.80 ± 0.48	3.22 ± 0.38
PP40PH	36.45 ± 0.54	4.19 ± 0.36

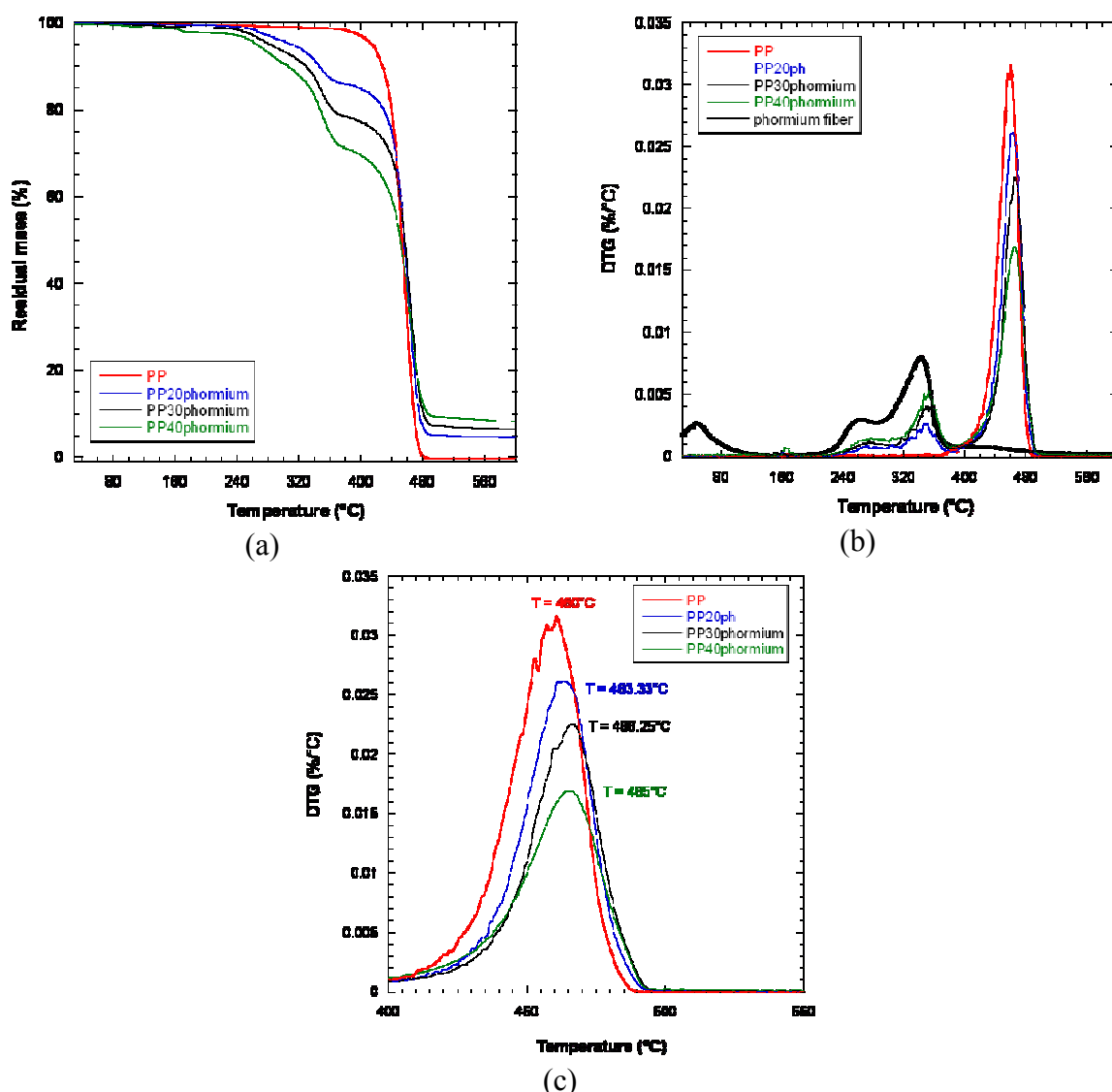
**Table 1.** Summary of mechanical properties of neat PP and PP/Phormium composites.

The morphology of the fracture surface of the injection- moulded specimens resulting from the tensile tests was investigated using SEM to characterize the fracture behaviour of PP/Phormium composites (Fig. 2a–f).



**Figure 2.** Scanning electron microscopy (SEM) images of (a, b, c, d, e) PP-40 wt% Phormium composites; (f) PP-30 wt% Phormium composites

From micrographs is evident that debonding and pull-out (figures 2a, 2b, 2c and 2f) dominate the fracture surface, thus confirming the poor interfacial bonding as proposed in the discussion on the mechanical properties. Phormium fibres show a clean surface and finite gaps near the interfacial region are present, indicating a poor adhesion between filler and matrix. It is also to be noted that a number of lumens appear to be completely filled (figure 2e) and the occurrence of some fibre breakage in the plane of fracture (figure 2 d-e), suggesting that some degree of adhesion has been achieved. Despite this, as a general comment, the interface would need to be optimized for a more effective use of the composite. The thermal stability of neat PP and PP-based composites was investigated in terms of weight loss as a function of temperature by thermogravimetric analysis. In figure 3, TGA thermograms and DTG curves are reported for PP and PP/Phormium composites.



**Figure 3.** Residual mass (a) and differential residual mass (b, c) obtained from the TGA analysis for neat PP, Phormium fibres and PP-based composites

In Phormium tenax fibres, the decomposition occurs in two main stage process, as shown in figure 3b [11]. The first stage process (200–305°C) is the thermal depolymerisation of hemicellulose, pectin and the cleavage of glycosidic linkages of cellulose [11], the second one (305–370 °C) is attributed to the decomposition of the  $\alpha$ -cellulose [11], whilst the decomposition of lignin occurred slowly within the whole temperature range. This was

attributed to the complex structure of lignin. Neat PP has the degradation peak at 460 °C: this was shifted to higher temperatures for the 20, 30, and 40 wt% PP/Phormium composites (figure 3c). Therefore, the system fibre–matrix degrades later than the neat resin. As a consequence, the thermal stability of the composite is slightly higher than that of fibre and matrix.

From the point of view of DSC characterization, the introduction of fibres did not result in a significant variation in the position of the peaks, except for the melting peak, which appears lower for the composites with respect to the pure matrix. A slight increase in crystallinity was also measured, due to the nucleating effect of fibres, as can be seen in figure 4, which shows DSC thermograms obtained from the cooling cycle ( $X_c$  ranged from 47.3% up to 58.4 % for the neat resin and PP-40wt% Phormium composites, respectively).

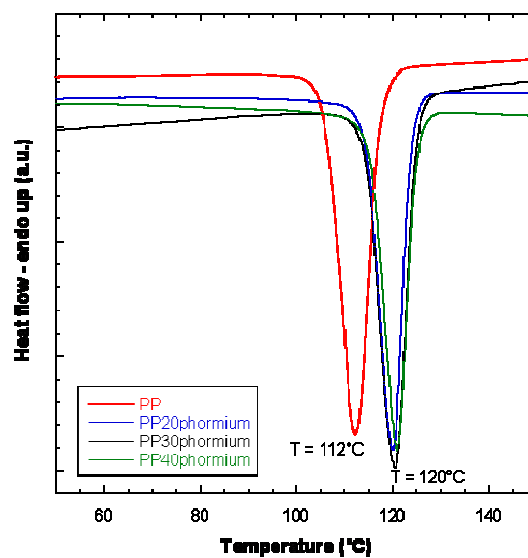


Figure 4. Heat flow for the cooling cycle obtained from the DSC for neat PP and PP-based composites

#### 4 Conclusions

This work on composites obtained introducing Phormium tenax fibres in a polypropylene matrix gives promising results for the applicability of these composites, where a larger stiffness and increased thermal stability are required. In general, using short Phormium fibres in a randomly oriented arrangement did result in a highly positive effect on composite tensile modulus and thermal stability, and in a limited modification of tensile strength and of the thermal profile of PP. The main area of concern for these composites appears to be represented by the need to improve the interface strength, since at higher fibre content a weak fibre–matrix link leads to diffuse fibre pull-out and debonding.

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