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# Biodegradable composites based on flax/polyhydroxybutyrate and its copolymer with hydroxyvalerate

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ABSTRACT

The present paper focuses on short flax fibre reinforced composites based on polyhydroxybutyrate (PHB) and its copolymer with hydroxyvalerate (HV). The effect of the fibre and copolymer content on the mechanical properties of the composites is being discussed. Furthermore, the influence of manufacturing method (compression moulding of non-woven mats and injection moulding of short fibre compounds) and processing conditions (cooling temperature and annealing) on the mechanical properties of the composites is being investigated. Finally, the biodegradability of the aforementioned composites expressed as weight, stiffness and strength loss as a function of burrier time is presented on the example of injection moulded flax/PHB/HV composites. It can be concluded that the addition of flax fibres along with controlled processing conditions seems to be a convenient way of toughening of the PHB matrix. Composites manufactured through injection moulding exhibited lower impact strength than those manufactured through compression moulding. Based on the biodegradation study of PHB/HV composites it can be concluded that the tensile properties drop significantly in the initial stage of degradation. The drop in tensile properties is more gradual in the later stages of biodegradation.

## 1. Introduction

Sustainability and eco-efficiency in technical applications has become quite important during the last two decades resulting from ecological concern, environmental awareness and new rules and regulations. In the area of polymer matrix composite materials, most work during the 1990s focused on replacing conventional fibres, like glass fibres with more environmentally friendly ones, like natural fibres (Peijs et al., 1998; Peijs, 2000; Joshi et al., 2004). PP undoubtedly has been one of the best candidates as matrix material for natural fibre reinforced composites because of its low price, thermal stability, and widespread use in technical applications, e.g. in the automotive industry. Numerous publications can be found on the effect of addition of natural fibres on the physical and mechanical properties of polymer matrix composites with focus on PP matrices (Heijenrath and Peijs, 1996; Peijs et al., 1998; Garkhail et al., 2000; Peijs, 2000; Stamboulis et al., 2000; George et al., 2001; Stamboulis et al., 2001; Singleton et al., 2003; Garkhail et al., 2009; Barkoula et al., 2009). The comparison of conventional glass fibre reinforced plastics with natural fibre reinforced ones has shown that the latter are competitive in both mechanical performance and price. This has led to the use of polyolefin based composites reinforced with natural fibres in the automobile industry (Eisele, 1994; Brouwer, 2001; Singleton et al., 2003; Karus et al., 2005). However, in terms of eco-efficiency polyolefins do not degrade via normal biodegradation process therefore its disposal requires dumping, recycling or incineration methods. Next to that, thermal degradation of the natural fibres during reprocessing makes mechanical recycling a less favourable option for natural fibre composites. For ultimate recyclability, recently single polymer composites based entirely on PP have been introduced (Alcock et al., 2006a,b, 2007). On the other hand, where recycling is not an option, biodegradability could be an eco-efficient solution for end-of-life disposal of polymer products. This has led to a shift in interest during the last decade towards composites where natural fibres are combined with biopolymers, which originate from renewable raw materials. Such composites are completely biodegradable and are often called “green composites” because of their environmentally beneficial properties (Mohanty et al., 2002; Oksman et al., 2005; Bax and Muessig, 2008; Vila et al., 2008). Generally, biopolymers are thermoplastic materials therefore offering advantages like low processing time, recyclability along with a feature of biodegradability. Apart from re-use or recycling, biocomposites offer additional recovery options, like composting. Being

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fully integrated into natural cycles or carbon dioxide ($CO_2$) neutral combustion, biocomposites also meet the steadily increasing environmental demands of legislative authorities.

Polymers from renewable resources can be classified into three groups: (1) natural polymers, such as starch, protein and cellulose; (2) synthetic polymers from natural monomers, such as polylactic acid (PLA); (3) polymers from microbial fermentation, such as polyhydroxybutyrate (PHB) (Yu et al., 2006). Recent review articles have been published on the potential of these materials in various applications (Gatenholm et al., 1992; Gatenholm and Mathiasson, 1994; Mohanty et al., 2000a, 2002; Velde and Kiekens, 2002; Shanks et al., 2004; Chiellini et al., 2004; Yu et al., 2006; Philip et al., 2007). Among other biodegradable polymers, PHB and its copolymers are of special interest, since PHB is highly crystalline polymer and has a melting point, strength and modulus comparable to those of isotactic polypropylene (Jiang et al., 2008).

## 2. Composites based on PHB and its copolymers

One of the major advantages of PHB is its biodegradability as it can be degraded to water and carbon dioxide under environmental conditions. Next to that, due to its polar nature, PHB shows better adhesion to natural fibres compared to polyolefins (Shanks et al., 2004). However, PHB is brittle and thermally instable during melt processing just above its melting point (Marchessault and Coulombe, 1981; Barham et al., 1984; Koning and Lemstra, 1993; Jiang et al., 2008). This is a major drawback for PHB, as careful control during processing is required to maintain its original molecular weight and properties (Marchessault and Coulombe, 1981). In order to reduce the thermal instability and brittleness of PHB, copolymers with hydroxyvalerate (HV) have been developed (Holmes, 1988; Mohanty et al., 2000a; Shanks et al., 2004; Yu et al., 2006; Philip et al., 2007; Jiang et al., 2008). It has also been shown that heat treatments (annealing) can be used to reduce the brittleness of PHB (Koning and Lemstra, 1993).

The addition of natural fibres and fillers has been also proposed as a solution for increased mechanical performance and toughness of PHB and its copolymers, as well as for lowering the price of otherwise expensive biodegradable polyester (Gatenholm et al., 1992; Avella et al., 1993, 2000; Gatenholm and Mathiasson, 1994; Bourban et al., 1997; Funke et al., 1998; Mohanty et al., 2000a,b,c; Shibata et al., 2002; Wong et al., 2002, 2007, 2004; Digabel et al., 2004; Fernandes et al., 2004; Shanks et al., 2004; Wu, 2006; Yu et al., 2006; Bodros et al., 2007; Buzarovska et al., 2007; Cyras et al., 2007; Jiang et al., 2008). These studies mostly discuss the effect of the fibre and/or HV addition on the crystallization and thermal behaviour as well as on the mechanical performance of the PHB based composites.

In terms of crystallization and thermal behaviour, no significant effect of cellulose on PHB polymer crystallinity was reported (Gatenholm et al., 1992; Avella et al., 1993; Luo and Netravali, 1999; Buzarovska et al., 2007). A slight increase of $T_g$ (glass-transition temperature) and delay in the crystallization process (Avella et al., 1993) was observed. The presence of wheat straw fibres increased the rate of PHB/HV crystallization, due to a nucleating effect, while the thermal parameters such as crystallinity remained unchanged (Avella et al., 2000). Similarly, Reinsch and Kelley (1997) reported increased crystallization in the presence of wood fibre in PHB/HV copolymers. Furthermore, recent studies on the crystallization behaviour of PHB/kenaf fibre model composites confirmed that the nucleation activity of kenaf fibres affected the crystallization kinetics of the PHB matrix (Avella et al., 2007). However, processing conditions practically did not influence the crystallization process, suggesting that certain processing conditions did not lead to degradation processes (Buzarovska et al., 2007). Differences in the effect of cellulose fibres on the crystallization process have been attributed to the presence or not of lignin in the cellulose fibre (Luo and Netravali, 1999).

Addition of HV, compatibilizers and natural fibres on PHB based composites, influenced the mechanical performance of the composites. The addition of cellulose fibres without the application of HV in the PHB led to some improvement in tensile strength and stiffness, but the composites remained brittle (Gatenholm et al., 1992). All composites were prepared with a co-kneader followed by injection moulding. The incorporation of cellulose fibres at low content lowered the stiffness, however higher amounts of cellulose fibres greatly improved the mechanical properties of PHB. The addition of HV led to a reduction in the stiffness of the PHB but to increased elongation at break. In PHB/HV reinforced with jute observations of 50–150% enhancement in tensile strength, 30–50% in bending strength and 90% in impact strength have been reported (Mohanty et al., 2000a,b). For short abaca fibres PHB composites the effect of fibre length, surface modification on the tensile and flexural properties has been investigated. Improved flexural strength and modulus with fibre content, especially in treated abaca fibres and direct comparison with GF/PHB composites were reported (Shibata et al., 2002). The surface treatment of abaca fibre was, however, not that effective for the improvement of tensile properties. Results on PHB reinforced with straw fibres have also been published (Avella et al., 1993). Fracture toughness values of composite materials containing 10 or 20 wt.% straw fibres were higher than those of neat PHB, while composite materials containing 30 and 50 wt.% straw fibres presented about the same values as neat PHB.

The addition of varying HV content to PHB polymers improved the toughness of the natural fibre composites and increased the ductility, but lowered the crystallization rate. It has been suggested however, that the combination of coupling agents and HV improved the storage modulus and let to a reduction in the tan $\delta$ (Shanks et al., 2004; Wong et al., 2004), due to an improvement in the interfacial bonding between PHB and the fibres and an increase in trancrystallinity near the fibre interfaces. The interfacial shear strength has been also improved with the addition of interface modifiers (Wong et al., 2007). PHB with 10–25 wt.% wood flour and plasticizers, presented modest increase in tensile strength, while some improvement in terms of thermal stability was demonstrated (Fernandes et al., 2004). Finally, the addition of natural fibres did not have a negative influence on the diodegradability of the composites (Bourban et al., 1997).

Since PP reinforced with flax is widely used in technical applications, it would be of special interest to replace this material with PHB reinforced with flax in the same application areas as the former. The literature found on flax/PP composites refers mainly on two manufacturing routes, (i) mat technology, where non-woven flax mats are compression moulded with PP to produce random natural fibre mat composites (NMTs) and (ii) the compound technology where flax fibre reinforced PP granules are injection moulded to produce short fibre reinforced composites. It is well known that the manufacturing method has a great influence on the remaining flax fibre length and length distribution, which in turn influences greatly the mechanical performance of the composite materials (Garkhail et al., 2000; Joshi et al., 2004; Barkoula et al., 2009). In the present study the influence of addition of flax fibres on the mechanical properties of PHB and PHB/HV copolymer are discussed and analysed. The effect of fibre and copolymer content as well as the processing conditions (cooling temperature and annealing) and processing methods (injection moulding and compression moulding) are being reported here on the aforementioned composite systems. Finally, the biodegradability of these composites is presented on the example of injection moulded flax/PHB/HV composites.

**Table 1**
Matrix materials used for the compounding of flax fibre composites and their basic properties.

| Material | Melting temperature (°C) | Molecular weight (g/mol) |
|---|---|---|
| PHB | 177 | 648,000 |
| PHB 8 wt.% HV | 153 | 553,000 |
| PHB 12 wt.% HV | 143 | 453,000 |

## 3. Experimental

### 3.1. Materials

In the current study, PHB in powder form and PHB/HV copolymers (Biopol™) in granule form both kindly supplied by Monsanto, Belgium, were used as matrix materials. Table 1 gives an overview of the basic properties of three different grades of PHB used. Flax fibres were kindly delivered by Ceres BV, Wageningen, The Netherlands. The fibres were in random mat form (650 g/m$^2$) with a length of approx. 25 mm and short chopped fibres with a length of approx. 10 mm.

### 3.2. Manufacturing

Two manufacturing routes, i.e. compression moulding and injection moulding were used to study the effect of manufacturing technology on the performance of the composites.

*3.2.1. Compression moulding*
Natural-fibre-mat-reinforced thermoplastics (NMT) composite plates, with different fibre contents (0, 20, 30, 40 vol.%), were manufactured using the film-stacking method. Films having thickness of approx. 1 mm were made in a temperature-controlled hydraulic press (Fontijne Holland, type TP400) by heating and compressing the copolymer granules for 5 min at 180 °C and a maximum pressure of 1.5 MPa. In this film-stacking method, predried randomly oriented, non-woven, flax fibre mats were stacked alternately with PHB or PHB/HV copolymer films to obtain a good fibre impregnation. All composite plates were heated for 12.5 min at a temperature of 180 °C and pressure of approx. 8.0 MPa. The pressure was increased in steps to avoid the presence of voids. To observe the effect of cooling temperatures the mould was cooled at two different temperatures, i.e. 20 °C and 60 °C. To reduce the influence of moisture, all materials were dried in an oven at 80 °C for at least 24 h before moulding.

*3.2.2. Injection moulding*
For the injection moulded samples, copolymer granules and short chopped flax fibres were used. The polymer granules and fibres were blended in a laboratory scale (60 cm$^3$) Haake Kneader (model-HBI System-90). Compounding was done at 30 rpm for 15 min at 170 °C. The mixed compound was granulated and injection moulded using an Arburg M270 injection moulding machine. Parameters used for the injection moulding of flax/PHB/HV are given in Table 2.

**Table 2**
Injection moulding process parameters for flax/PHB/HV.

| | |
|---|---|
| Temp. zone 1 (°C) | 160 |
| Temp. zone 2 (°C) | 165 |
| Temp. zone 3 (°C) | 170 |
| Temp. zone 4 (°C) | 175 |
| Temp. zone 5 (°C) | 180 |
| Injection pressure (bar) | 750 |
| Cooling time (s) | 12 |
| Temp. of the mould (°C) | 60 |

### 3.3. Testing methods

*3.3.1. Tensile testing*
Tensile tests were performed on a Frank 81565 tensile testing machine at a cross-head speed of 4.8 mm/min according to ASTM D 638 method. Tensile property evaluations were carried out at ambient temperature. All samples were stored for at least 24 h before testing. In the case of NMT samples, the tensile tests were performed on test bars with rectangular cross-section and dimensions of 150 mm × 20 mm × 2 mm. For injection moulded samples the test bars were dumbbell shaped with dimensions according to standard ASTM D638 (150 mm × 10 mm × 3.5 mm). An extensometer was used to monitor the elongation of all tested specimens.

*3.3.2. Impact testing*
Izod impact tests were conducted on notched samples having dimensions of approx. 60 mm × 12.7 mm × 2 mm and notch dimensions according to the American standard ASTM D256. At least five specimens were tested for each composition and fibre content.

*3.3.3. Fracture surface analysis*
The fractured surface of the composites was observed through scanning electron microscope (SEM), Cambridge Stereoscan 200. For the same, the samples were coated with gold/palladium.

*3.3.4. Dynamic mechanical thermal analysis (DMTA)*
DMTA (Polymer Laboratories DMTA, MK III) tests were performed on compression moulded specimens in order to investigate the effect of the cooling temperature on the glass-transition temperature. The samples were analysed in tensile mode at a frequency of 1 Hz, a heating rate of 2 °C/min and temperature range between −20 °C and 100 °C.

*3.3.5. Biodegradation*
Injection moulded samples of flax/PHB/HV (8 wt.% HV) reinforced with 20 vol.% flax were buried in open soil at a depth of approximately 25 cm. Prior to burying the weight of each specimen was determined. At regular intervals of 4 weeks a tensile bar was dug up, cleaned, dried for 3 days at 80 °C and stored at room temperature for another 3 days. After that the weight of the bar was determined. Finally a tensile test was performed on the sample at a cross-head speed of 4.8 mm/min.

## 4. Results and discussions

### 4.1. Mechanical properties of flax/PHB NMT composites

Fig. 1a–d shows the mechanical properties of the flax/PHB NMT composites manufactured through compression moulding process, as a function of the fibre volume fraction. For comparison, the tensile stiffness and strength data of short fibre flax/PP (Garkhail et al., 2000) and glass-mat-reinforced thermoplastic (GMT) (Garkhail et al., 2000) composites are also plotted.

As can be seen in Fig. 1a the stiffness of the composite materials increases with the fibre content. Although the stiffness of the flax/PHB composites is lower than that of the flax/PP and GMT composites at low fibre contents (<30 vol.%), for higher fibre contents, flax/PHB composites compete quite well with the aforementioned commercially available polyolefin based composites. Upon fibre addition, a small reduction in the flax/PHB composite strength was followed by a small increase at higher volume fractions (Fig. 1b). Overall, it should be noted that this effect is not significant.

It is well known that the fibre diameter, fibre length and fibre/matrix adhesion are of key importance in discontinuous fibre reinforced composites, for effective use of the fibre intrinsic properties (Oever and Bos, 1998). The interrelation between these

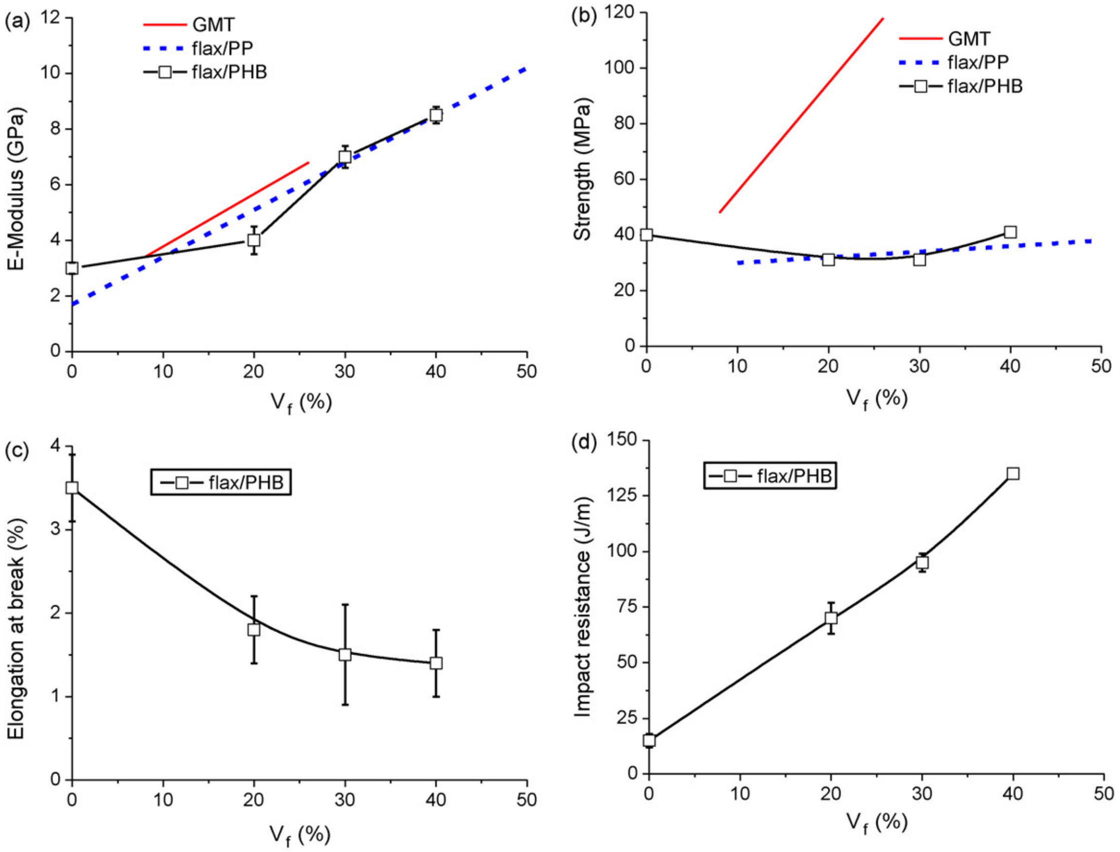

**Fig. 1.** (a) Young's modulus, (b) tensile strength, (c) elongation at break and (d) Izod impact resistance of flax/PHB NMT composites as a function of fibre volume fraction (a and b: comparison with flax/PP NMT and GF/PP (GMT) composites; Garkhail et al., 2000).

parameters has been already described by several micromechanical models and is different for stiffness, strength and impact properties. Thorough analysis on the influence of fibre length and concentration on the stiffness and strength of GF/PP (Oever and Peijs, 1998; Thomason and Vlug, 1996; Thomason et al., 1996) and flax/PP composites (Nechwatal et al., 2005; Barkoula et al., 2009) has shown that the required fibre length to reach maximum stiffness is much lower than that required for maximum strength. A similar analysis (Vila et al., 2008) showed that the required fibre length for optimum stiffness is approx. 1 mm, while the respective length for optimum strength is app. 8 mm (8× higher fibre length needed for strength improvement). This might explain why the addition of flax fibre influences the stiffness of the composite systems, while the strength remains almost unchanged. Another reason for the observed trend could be imperfect bonding between fibre and matrix and therefore fibres may act as crack initiators. Finally, the presence of woody parts in flax fibre mats or transverse splitting of the technical fibre bundles, might act as crack initiator leading to a reduction in strength which is probably compensated for an increase in reinforcement at higher volume fractions of fibres.

Fig. 1c shows the elongation at break of flax/PHB NMT composites as a function of fibre volume fraction. Addition of flax results in a lower elongation at break of the composites, i.e. approx. 1.5% for all fibre volume fractions. Flax fibres have low elongation at break of approx. 1.7% (Peijs et al., 1998) therefore addition of these fibres constrains the elongation of the plastic matrix.

Finally, Fig. 1d shows the influence of fibre content on the notched Izod impact strength of flax/PHB NMT composites. The impact energy absorption increases with increasing flax fibre content leading to toughening of the brittle PHB. The increase is most probably due to fibre debonding and fibre pull-out mechanisms, which are prominent in systems with weak bonding between fibre and matrix. This is also observed through the SEM pictures of the fracture surface of the tensile specimen, as shown in Fig. 2. The phenomenon of PHB toughening through addition of flax fibres is quite an interesting approach as far as cost-performance of this polymer is concerned. Addition of cheaper fibres not only reduces the cost of the polymer but also improves the impact properties of PHB, which is quite important considering the brittle nature of the polymer.

### *4.2. Influence of HV and fibre content on the mechanical performance of flax/PHB based NMT composites*

Fig. 3a–d shows the mechanical response of different grades of PHB/HV as a function of fibre volume fraction. All composites were manufactured by the compression moulding method.

As can been seen in Fig. 3a, the addition of HV copolymer lowers the stiffness of the composite systems since the increase in the HV content leads to lower crystallinity. The increase in fibre content leads to a rapid increase of the E-modulus. The effect of HV content on copolymer stiffness is also reflected in the composite properties as copolymer based composites exhibit lower stiffness when compared with the stiffness of the native flax/PHB composites.

Similar observations are made when the strength of the tested systems is considered (Fig. 3b). In comparison with native PHB the copolymer based composites have a somewhat lower strength, around 30 MPa. Similar to previous observations, the strength of the flax/PHB/HV composites is almost constant with increasing fibre volume fraction.

Fig. 3c shows the effect of HV content on the elongation at break of the flax/PHB/HV composites. At low fibre contents (<20 vol%.) the elongation at break of the copolymer based composites is

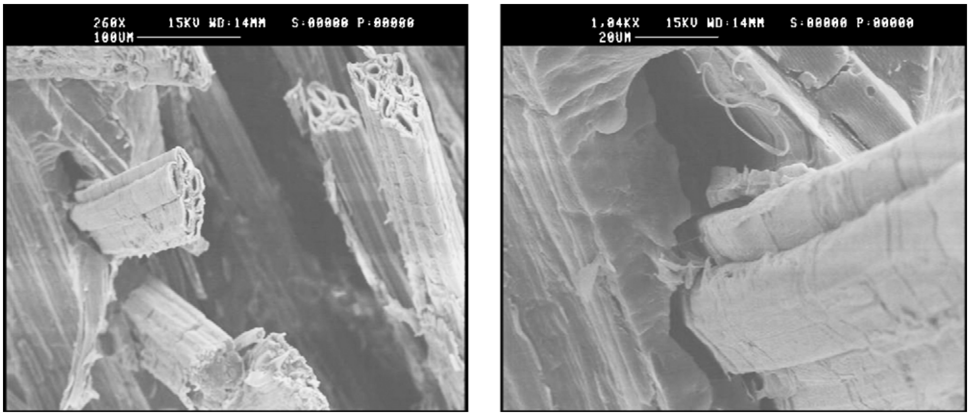

**Fig. 2.** SEM pictures of impact fracture surface of flax/PHB NMT composites, showing pull-out of flax fibre bundles.

higher than that of native PHB based systems. The initial value of elongation at break of neat PHB is 3.4% whereas the copolymers have an elongation at break of around 10%. The higher elongation of the copolymers can be explained through the lower crystallinity with the increased amount of HV. Further addition of flax is masking the benefit of the HV copolymers and reduces the elongation at break to approximately 1.5% for all flax/PHB systems.

Finally, Fig. 3d shows the notched Izod impact resistance of flax/PHB/HV NMT composites. At low fibre contents (<30 vol.%) the impact resistance of the flax/PHB composites improved with the addition of HV copolymers. PHB is more crystalline than the copolymers therefore it is more brittle than the latter. The addition of fibre however reverses this trend, i.e. at fibre contents >30 vol.% composites based on pure PHB have higher impact resistance than composites based on copolymers. The difference in impact strength of composites based on PHB and copolymer is probably due to the differences in the wetting between fibres and the matrix. Since copolymers have a lower melting point they might have a lower viscosity leading to improved wetting of the flax fibres at the processing temperature of PHB. This improved wetting for copolymers might lead to lower impact strengths when compared to PHB based composites. As the fibre volume fraction increases the effect of wetting also increased, which might have led to higher impact strength of PHB based composites as compared to copolymer based composites.

Based on the above results it can be said that the addition of cheap flax fibres (approx. 0.15€/kg; Mackiewicz-Talarczyk et al.,

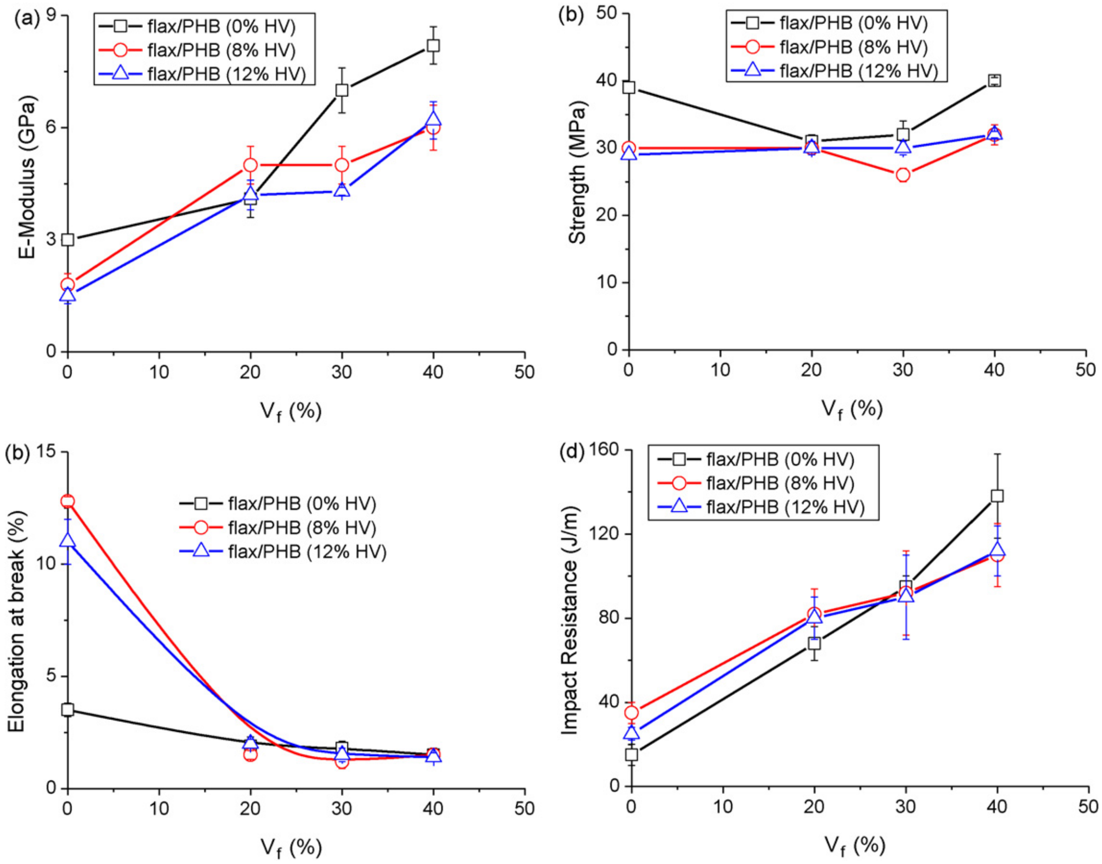

**Fig. 3.** Effect of fibre and HV content on (a) Young's modulus, (b) tensile strength, (c) elongation at break and (d) Izod impact resistance of flax/PHB/HV composites.

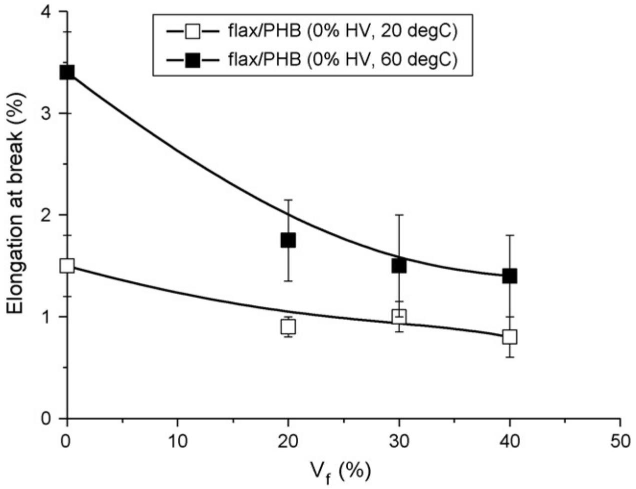

**Fig. 4.** Elongation at break of flax/PHB NMT composites as a function of fibre volume fraction and cooling temperature during compression moulding.

2008) to a fairly expensive and brittle PHB/HV composite (approx. 5€/kg; Lemstra, 2009) leads to enhanced toughness of the composites, while at the same time reducing its cost by approx. 40% (for 40 wt.% fibre reinforcement). It should be noted however, that this analysis considers purely materials costs and does not incorporate any processing costs. It costs definitively more to process the composite systems than the neat PHB/HV systems. However, this cost can be reduced upon selection of the right manufacturing technology, production size and rate.

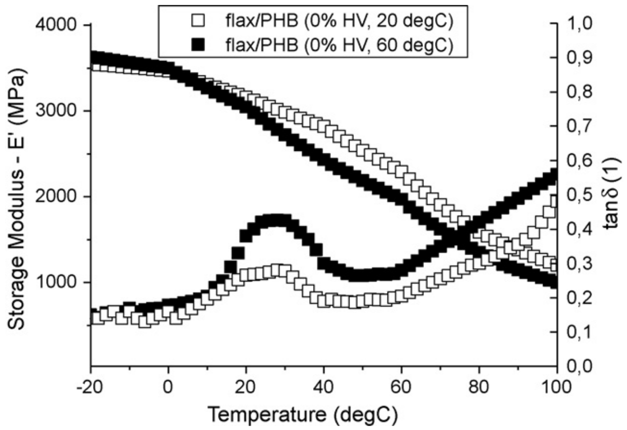

**Fig. 5.** Dynamic mechanical characteristics versus temperature for compression moulded flax/PHB samples, which were cooled at 20 °C and 60 °C (mould temperature).

### 4.3. Effect of processing conditions on the mechanical performance of flax/PHB based NMT composites

Fig. 4 shows the elongation at break of compression moulded flax/PHB NMT composites with different fibre content at different cooling temperatures. As seen in this graph, the elongation at break of composites cooled at 20 °C is lower than the samples cooled at 60 °C. Dynamic mechanical thermal analysis (DMTA) was carried out to determine the differences in dynamic mechanical properties and loss factor. Fig. 5 shows the dynamic mechanical characteristics of PHB samples cooled at 60 °C and 20 °C. The samples cooled

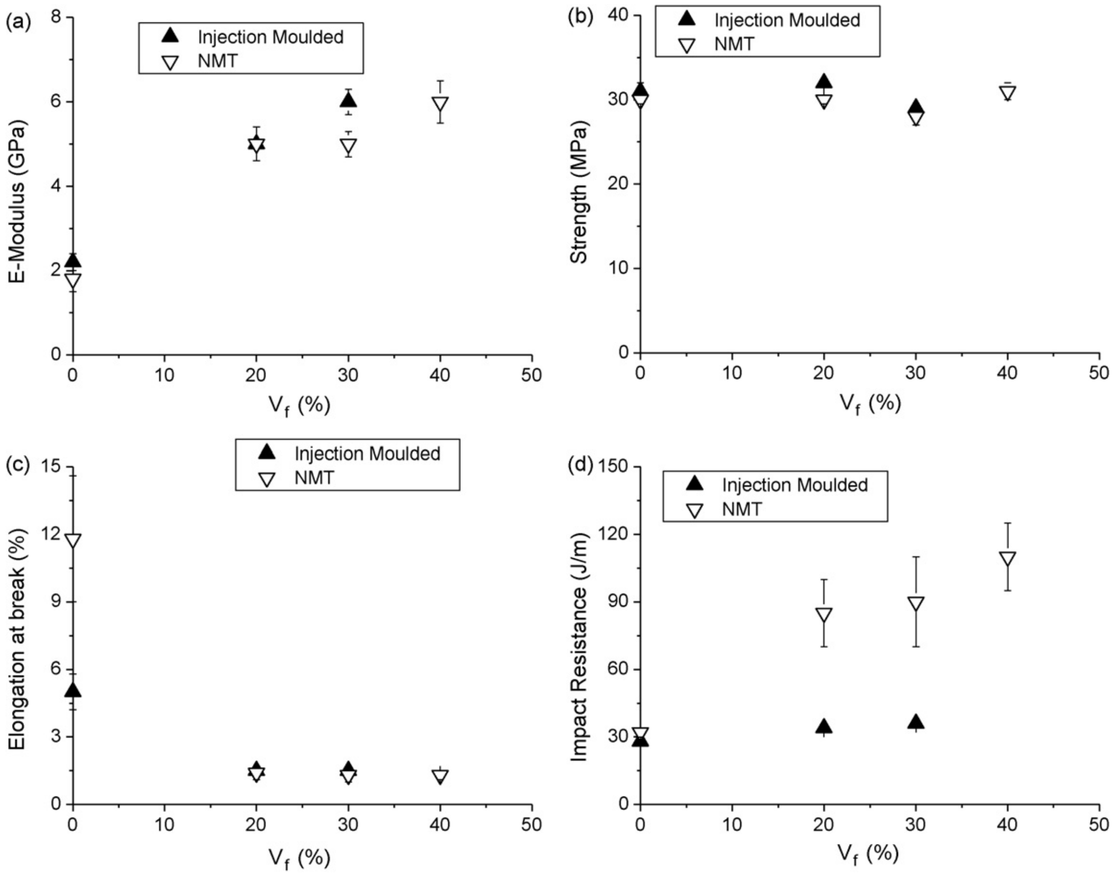

**Fig. 6.** (a) Young's modulus, (b) tensile strength, (c) elongation at break and (d) Izod impact resistance of flax/PHB composites as a function of fibre volume fraction and manufacturing method.

**Fig. 7.** Pictures of different stages of biodegradation of flax/PHB/HV (8 wt.%) composites with 20 vol.% fibre after burial in soil.

at 60 °C show a higher loss factor (tan $\delta$) which could be either down to a higher amorphous content (lower crystallinity) or higher relaxation of the amorphous zone. From these results it can be mentioned that relaxation of the amorphous zone due to cooling at 60 °C plays a dominant role in enhancing the elongation of the polymer as well as composites. Similar results were reported by Koning and Lemstra (1993) where annealing of PHB not only enhanced the crystallinity but also improved the toughness through increased relaxation of the amorphous phase.

### 4.4. *Effect of manufacturing technology on the mechanical performance of flax/PHB based composites*

As aforementioned, the manufacturing method employed is expected to influence the performance of flax/PHB based composites, since it influences the remaining fibre length and fibre length distribution in the composite systems. Next to fibre breakage, compounding may also separate the technical cellulose fibres into finer elementary fibres (Snijder et al., 2003) through fibre opening mechanisms, which can lead to higher fibre aspect-ratios and improved fibre efficiency.

Fig. 6a–c illustrates this effect on the stiffness, strength and elongation at break of compression moulded and injection moulded samples. As shown in Fig. 6a–c, no significant effect of processing methods, on the stiffness, strength and elongation of the composites is being observed. These results are similar to the ones shown in a recent publication (Barkoula et al., 2009) where no effect of fibre length reduction, through injection moulding, on the strength and stiffness of flax/PP composite was observed.

For better understanding of these results, the critical fibre length ($L_c$) based on the Kelly–Tyson theory (Kelly and Tyson, 1965) is being calculated:

$$L_c = \frac{\sigma_f d}{2\tau}$$

where $\sigma_f$ is the fibre strength, $d$ is the fibre diameter, and $\tau$ is the interfacial bond strength. For the critical fibre length calculations the following data are being used based on literature: the strength of the technical flax fibre is 800 MPa (Heijenrath and Peijs, 1996; Bos et al., 2002), while that of an elementary fibre is 1500 MPa (Singleton et al., 2003; Yu et al., 2006), for fibres with 80 μm and 12.5 μm diameter, respectively. In a separate study Lee et al. (2003) studied the effect of surface modification on the interfacial shear strength of flax/PHB composites and reported data on the interfacial shear strength equal to 8.8 MPa in the case of the untreated flax fibre PHB composites. Based on these values a critical fibre length of 3.6 mm for the technical fibre and of 1.1 mm for the elementary fibre is calculated.

It was demonstrated recently on flax/PP composites that kneader compounding followed by injection moulding reduced the average fibre length from ~10 mm to ~1 mm, with compression moulded samples having fibre length ~25 mm (Barkoula et al., 2009). The results presented in Fig. 6a–c indicate that in case of injection moulded samples, technical fibres have been separated into elementary fibres (smaller diameter), which led into a much smaller critical fibre length required for a reinforcing effect. Injection moulding has some advantages like lower production time and higher reproducibility along with a disadvantage of reduced composite fracture toughness. As shown in Fig. 6d, samples made through injection moulding showed lower impact resistance which is probably due to the reduced amount of fibre pull-out and energy absorption through fibre fracture. As the fibre length in injection moulded composites reduces to lengths close to or below the critical fibre length (Barkoula et al., 2009), the energy absorption through fibre fracture is also reduced, as compared to compression moulded composites with fibre lengths well above the critical length (Fig. 6d).

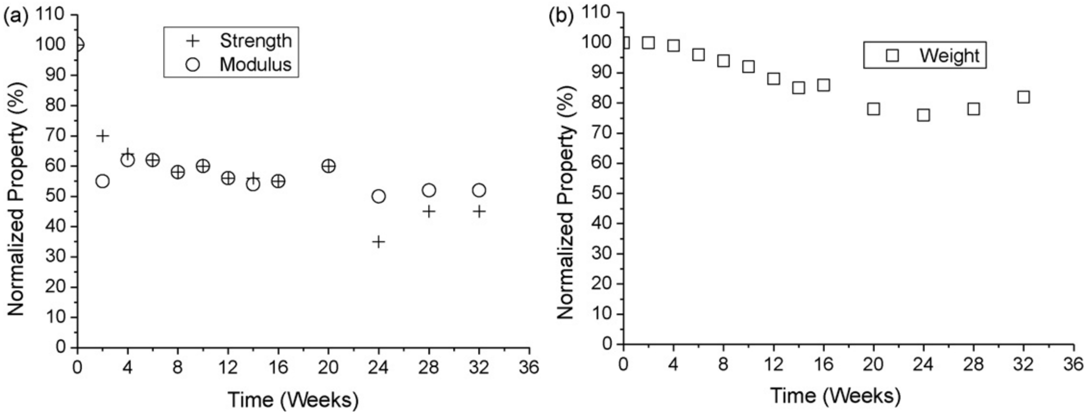

**Fig. 8.** Normalised (a) Young's modulus and strength and (b) weight of flax/PHB/HV (8 wt.%) composites after burial in soil.

### 4.5. Biodegradation

Tensile bars of flax/PHB/HV (8 wt.%) composites, manufactured by injection moulding and having dog-bone shape, were buried in open soil to study the effect of biodegradation on composite properties. Fig. 7 shows the pictures of tensile bars after several weeks of burying in the open soil. During the first 2 weeks after burial both tensile modulus and tensile strength decreased sharply, whereas beyond this period the properties of the composite seemed to stabilise. The observed trend is shown in Fig. 8a. In contrast to this the mass decreased continuously during the first 20 weeks of burial, indicating biodegradation of the material, even in these non-optimised conditions. The effect of burial (degradation) on the normalised weight of flax/PHB/HV (8 wt.%) composites is shown in Fig. 8b. The observed differences in the effect of burial on tensile properties (Fig. 8a) and normalised weight (Fig. 8b) indicate that the initial drop, in modulus and strength of the composites, is not due to biodegradation or weight loss. The initial drop in modulus and strength may result from debonding due to moisture absorption in the first 2 weeks. After this initial drop in tensile properties the further effect on the tensile properties due to degradation was more gradual.

## 5. Conclusions

The present paper studied the mechanical behaviour of flax fibre reinforced composites based on PHB and its copolymer with HV. The effect of the fibre and copolymer content on the mechanical properties of these composites was investigated and presented. Furthermore, the influence of the manufacturing technology (compression moulding of non-woven mats and injection moulding of short fibre compounds) and that of processing conditions (cooling temperature and annealing) on the mechanical properties of the composites was also analysed.

Although an increase in stiffness with the addition of fibres was documented, no significant influence was observed on the strength of the composites. This needs to be further optimised through modifications in fibre opening process (cleaning through carding and combing processes) and/or through modification of the fibre–matrix interface. Furthermore, optimisation of processing conditions like cooling temperature can improve the properties of flax/PHB composites through increased relaxation of the amorphous phase. Addition of HV has been considered as one of the ways to overcome the brittleness of PHB. However, this comes at a cost as these copolymers are more expensive than homopolymer PHB. Keeping in view the above mentioned shortcoming of PHB and its copolymer PHB/HV, addition of flax fibres along with controlled processing conditions seems to be a convenient and cost-effective way of toughening of native PHB. In terms of the effect of the manufacturing method on the end properties, it was shown that injection moulding may be advantageous over compression moulding because of shorter cycle times and higher reproducibility. However, composites manufactured through injection moulding exhibited lower impact strength than those manufactured through compression moulding because of the shorter fibre lengths. Finally, based on the biodegradation study of PHB/HV composites it can be concluded that the tensile properties drop significantly in the initial stage of degradation, which could be due to fibre debonding.

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