

# THERMOPLASTIC COMPOSITES BASED ON BIOPOLYMERS AND NATURAL FIBRES

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**SUMMARY:** The objective of the present research is to utilise the advantages offered by renewable resources for the development of biodegradable composite materials. Two types of biocomposites using flax fibres as a reinforcement and poly[(R)-3-hydroxyalkanoates] (PHA) as a biodegradable polymer matrix were manufactured: First, natural-fibre-mat-reinforced thermoplastics (NMTs) using a compression moulding method and needle-punched nonwoven flax fibre mats and secondly, injection moulding compounds based on short flax fibres. The influence of fibre content and processing method on the tensile and impact properties of these composites was studied. Results indicated that the addition of (cheap) flax fibre to poly(3-hydroxybutyrate) (PHB) could be advantageous as far as cost-performance of these materials is concerned. For example, the addition of flax fibres to the relatively brittle PHB matrix offers the chance to obtain cheaper products together with improved toughness, while retaining biodegradability of the resulting polymer composites. Especially in the case of relatively long fibres as in the case of NMTs the improvement in impact resistance is significant. Regarding the influence of processing method it was observed that, with the exception of impact resistance, injection moulded samples possessed similar properties to NMT samples, indicating that for some applications injection moulding might be advantageous over NMT because of the more versatile production process.

**KEYWORDS:** natural fibres, biopolymers, flax fibre, polyhydroxybutyrate, biodegradable composites, biocomposites.

## INTRODUCTION

Environmental legislation as well as consumer pressure are all increasing the pressure on manufacturers of materials and end-products to consider the environmental impact of their products at all stages of their life-cycle, including ultimate disposal, viz. a ‘cradle to grave’ approach. At this moment ‘eco-design’ is becoming a philosophy that is applied to more and more materials and products. In view of this natural fibres based on lignocellulose, such as flax, hemp, jute and sisal have received considerable attention as an environmentally friendly

alternative for the use of glass fibres in engineering composites [1-6]. These vegetable fibres have a number of techno-ecological advantages over traditional glass fibres since they are renewable, can be incinerated with energy recovery, show less concern with safety and health (e.g. skin irritations) and give less abrasive wear to processing equipment such as extruders and moulds. Moreover, natural fibres are CO<sub>2</sub> neutral and the amount of energy needed for their production is less than that of glass fibres. In addition, they exhibit excellent mechanical properties, especially when their low density (1.4 g.cm<sup>-3</sup> versus 2.5 g.cm<sup>-3</sup> for glass) and price are taken into account. Up to now most of the studies in the area of natural fibre composites have been focusing on the use of polypropylene as a matrix [3-6]. Polypropylene (PP) offers a number of favourable characteristics for high volume applications because of its low price, high toughness and low density. Moreover, PP can easily be processed and recycled and upgrading *via* the use of glass-fillers has been very successful in bridging the gap between the commodity PP and the engineering thermoplastics. Similar to the developments in the area of glass-fibre-reinforced polypropylenes, research in the area of natural-fibre-reinforced polypropylenes focused basically on two types of composite systems. First, short-fibre-reinforced injection moulding compounds and secondly, natural-fibre-mat-reinforced thermoplastics (NMTs) [3,5,6], being stampable sheet products based on nonwoven fibre mats. The latter, being the natural fibre counterpart of the glass-mat-reinforced thermoplastics (GMTs), which have proven to be very successful in the automotive industry [7].

Although natural fibres have a number of ecological advantages over glass fibres they also possess a number of disadvantages, such as poor moisture resistance (rotting) [6], poor dimensional stability (swelling), leading to microcracking, as well as poor thermal stability, which may lead to thermal degradation during (re)processing. From a mechanical recycling point of view, thermal degradation during reprocessing is an important disadvantage of natural fibres, especially when combined with a matrix like polypropylene. In the case of a well recyclable polymer like PP the addition of natural fibres will strongly affect the recyclability and hence the eco-performance of the resulting composite material. Therefore, whenever mechanical recycling should be favoured it remains to be seen if natural fibre composites are the best alternative. As such the development of a single polymer composite based on PP fibres in a PP matrix might be a more promising approach for the future. An interesting alternative, however, which makes full use of the renewable and biodegradable character of natural fibres, is the development of a fully biodegradable composite based on renewable resources [8-11]. Biopolymers like poly(3-hydroxybutyrate) (PHB), polylactic acid (PLA) and starch are some of the candidates to serve as matrix system for fully biodegradable composite materials. Generally, biopolymers are thermoplastic materials therefore offering advantages like short processing time, recyclability along with a feature of biodegradability. Apart from re-use or recycling, biocomposites offer additional recovery options, like composting, being fully integrated into natural life-cycles.

In this study flax fibres are used as reinforcement and PHB was selected as a matrix material. Apart from the advantages related to biodegradability and biocompatibility, PHB offers some other advantages like:

- PHB is hydrophobic, therefore protects the natural fibre from moisture attack.
- PHB is a linear saturated polyester, which can be processed as a regular thermoplastic at relatively low temperatures, thus thermal degradation of the natural fibre can be avoided.
- The mechanical properties of PHB are comparable to PP.

Drawbacks of PHB are their poor thermostability and their low impact resistance. Similar to natural fibres these polyesters will show thermal degradation at elevated temperatures. In the case of PHB thermal degradation will occur at temperatures above 170-180°C. The poor toughness of PHB originates from the relatively high glass transition temperature and its tendency to form large spherulites. As a result poly(3-hydroxybutyrate-co-hydroxyvalerate) (PHBV) copolymers have been developed, although the increase in toughness in these copolymers is obtained at the expense of melting temperature and stiffness. Another important aspect that has prevented PHB from being successful is its high costs. As such the addition of cheap (biodegradable) fillers is of interest since it may lead to cheaper products together with improved mechanical performance, while retaining biodegradability. In the present paper the influence of the addition of green flax fibres on the properties of PHB and PHBV copolymer is studied. Two types of processing methods were used for the production of these biocomposites: injection moulding and NMT compression moulding.

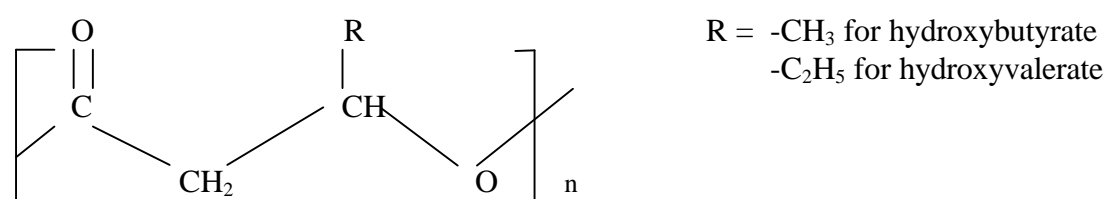
## EXPERIMENTAL

### Materials

Investigations were made on native PHB polymer as well as PHBV copolymers (Biopol™). The copolymers in granule form and pure PHB in powder form were all kindly supplied by Monsanto (Belgium). In Table 1, the melting temperature and molecular weight of the biopolymers used, is listed. Figure 1 shows the chemical structure of polyhydroxyalkanoates (PHA) in general.

*Table 1: Properties of polyesters used.*

Polymer	Grade	Melting Temperature ( °C )	Molecular Weight (g.mole <sup>-1</sup> )
PHB	D000P	177	648,000
PHB/ 8% HV	D400GN	153	553,000



*Fig. 1: Chemical structure of Polyhydroxyalkanoate (PHA).*

The green flax fibres were kindly supplied by Ceres BV (Wageningen, the Netherlands). The fibres were in needle-punched nonwoven form and the short chopped fibres had a length of approximately 10mm.

### *Natural-fibre-mat-reinforced thermoplastics (NMT)*

Natural-fibre-mat-reinforced thermoplastics (NMT) plates with different fibre content were manufactured using compression moulding. In the case of native PHB/flax NMT composites,

the calculated weight of PHB powder was spread on the layers of fibre mats followed by compression moulding. The copolymer PHBV/flax NMT composites were manufactured by a film-stacking method. Biopolymer films having a thickness of approximately 1 mm were made in a hot-press by heating and compressing the granules for 5 minutes at 180°C and a maximum pressure of 1.5 MPa. In the film-stacking method, randomly oriented needle-punched green flax nonwoven mats were stacked alternately with PHBV copolymer films to obtain a good fibre impregnation. To reduce the influence of moisture, all materials were dried in an oven at 80°C for at least 24 hours before moulding. All composite plates were heated for 12 minutes at a temperature of 180°C and a pressure of about 8 MPa. The pressure was increased in steps to avoid the presence of air-bubbles and voids. The mould was cooled at 60°C. All the composite plates were stored at ambient temperatures for 24 hours before testing.

### *Short-fibre-reinforced thermoplastics*

To study the effect of processing method and effect of fibre length, test specimen were also made using injection moulding. For the same, copolymer granules (PHB/8%HV) and short chopped green flax fibres, having a length of about 10 mm length, were used. The polymer granules and fibres were blended for 15 minutes at 170°C in a mixer (Haake System 90) running at 30 rpm. The mixed compound was subsequently granulated and injection moulded using an Arburg M270 injection-moulding machine. Processing specifications were: temperature zone 1 to 5 (inclusive): 160°C, 165°C, 170°C, 175°C, 180°C, injection pressure: 750 bar, mould temperature: 60°C and cooling time: 12 seconds.

### **Test methods**

Uniaxial tensile tests on compression moulded NMT composites and injection moulded short-fibre-reinforced plastics were performed on a Frank tensile testing machine (type 81565). The tests were performed at room temperature at a test-speed of 5 mm.min<sup>-1</sup>. The dumbbell shaped test specimens had dimensions of 150x10x3.5 mm according to ASTM standard D638M. An extensometer was used to monitor the elongation of the specimen. The Young's modulus, tensile strength and strain-at-break were calculated from the recorded stress-strain curves. Impact resistance of the samples was measured using Izod impact testing. The tests were performed on the notched samples having dimensions of 60x12.7x2 mm and notch dimensions according to the American standard ASTM D256.

## **RESULTS AND DISCUSSIONS**

### **Natural-fibre-mat-reinforced thermoplastics (NMTs)**

Figure 2 shows the tensile strength of the PHB/flax NMT composites manufactured through compression moulding, as a function of the fibre volume fraction. The tensile strength of PP/flax NMT and glass-mat-reinforced thermoplastics (GMTs) taken from reference 5 and 7 are also plotted. On fibre addition, in the case of PHB/flax a small drop in strength is followed by a small increase at higher volume fractions. A possible explanation for this might be the presence of woody particles in the flax fibre mat, which may act as crack initiators leading to a decrease in strength. Especially in the case of a fairly brittle matrix system like PHB the introduction of woody particles may lead to an initial drop in strength. This effect is probably compensated for by a reinforcing effect of the fibres at higher fibre volume fractions. Above a fibre volume fraction of 20% the strength increases at a similar rate as for PP/flax. Overall,

however, no significant effect of fibre addition on the composite tensile strength was observed and tensile strength values are well below those of GMT. In order to be able to compete with GMT on a strength basis, the strength of the flax fibre rather than that of the interface need to be further optimised through modification of the fibre opening processes.

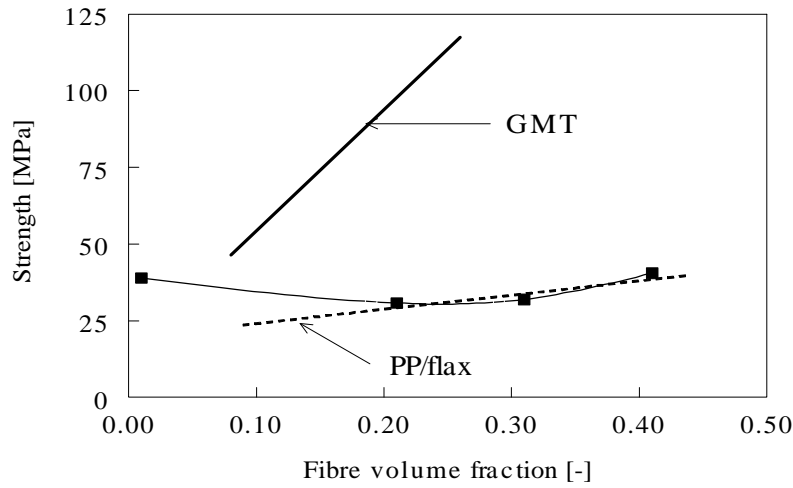


Fig. 2: Tensile strength of PHB/flax NMT (■), PP/flax NMT and GMT composites.

Figure 3 shows the Young's modulus of the manufactured PHB/flax composites as a function of the fibre volume fraction. For comparison, the stiffness data of PP/flax NMT and GMT are also plotted [5,7]. As expected, the stiffness of the composites increases with fibre content. This shows that factors like weak bonding and presence of woody particles are not as critical for stiffness as they are for strength enhancement.

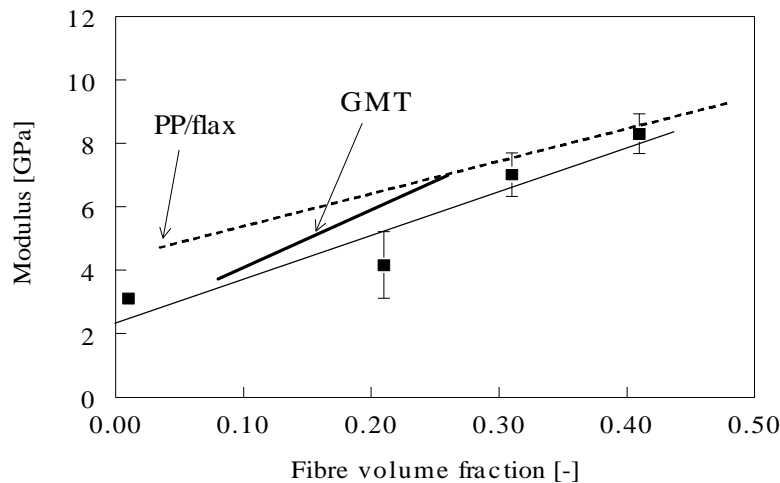
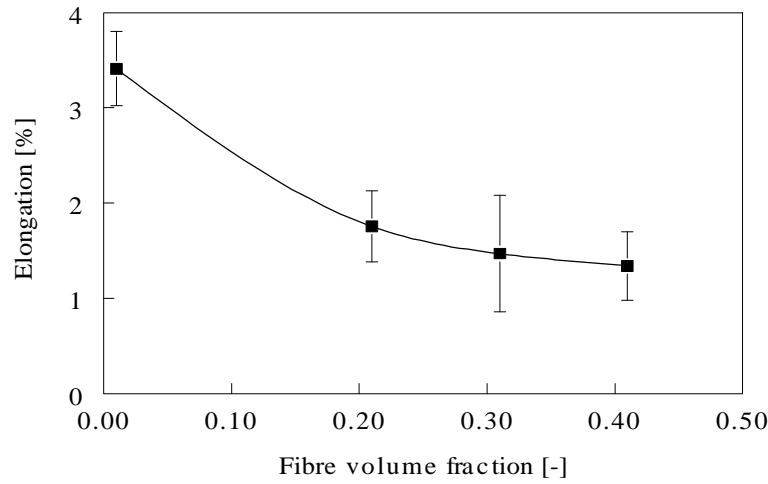


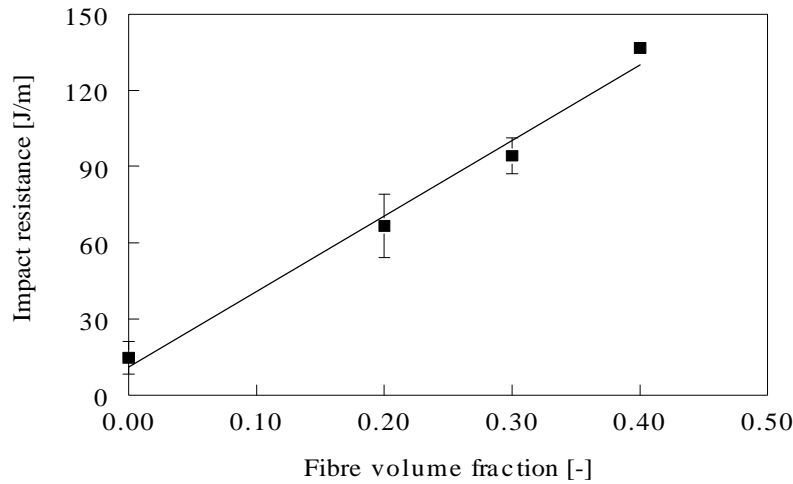
Fig. 3: Young's modulus of PHB/flax NMT (■), PP/flax NMT and GMT composites.

Figure 4 shows the elongation-at-break of PHB/flax NMT as a function of fibre volume fraction. Addition of flax results in a significant drop in elongation-at-break of the composites, i.e. approximately 1.5% for all fibre volume fractions. Compared to the biopolymer matrix, flax fibres have a relatively low elongation-at-break of approximately ~1.7% (at a gauge length of 5 mm) and therefore addition of these fibres constrains the elongation of the matrix.



*Fig. 4: Elongation-at-break of PHB/flax NMT (■) as a function of fibre volume fraction.*

Figure 5 shows the influence of fibre content on the notched Izod impact resistance of PHB/flax NMT. The impact energy increases with increasing flax fibre content, therefore leading to an interesting toughening mechanism of the brittle PHB. The increase in energy absorption is probably due to extensive fibre pull-out, which is prominent in a composite system with relatively weak bonding between fibre and matrix. Extensive fibre pull-out and weak bonding was also observed through the SEM (Scanning electron microscope) pictures of the fracture surface of the impacted specimens, as shown in Figure 6. Despite the fact that flax fibres have chemically active hydroxyl groups and the PHB matrix contains C=O groups, which in principle could lead to the formation of hydrogen bonding, the PHB/flax composites did not show very good bonding.



*Fig. 5: Notched Izod impact resistance of PHB/flax NMT (■) composites.*

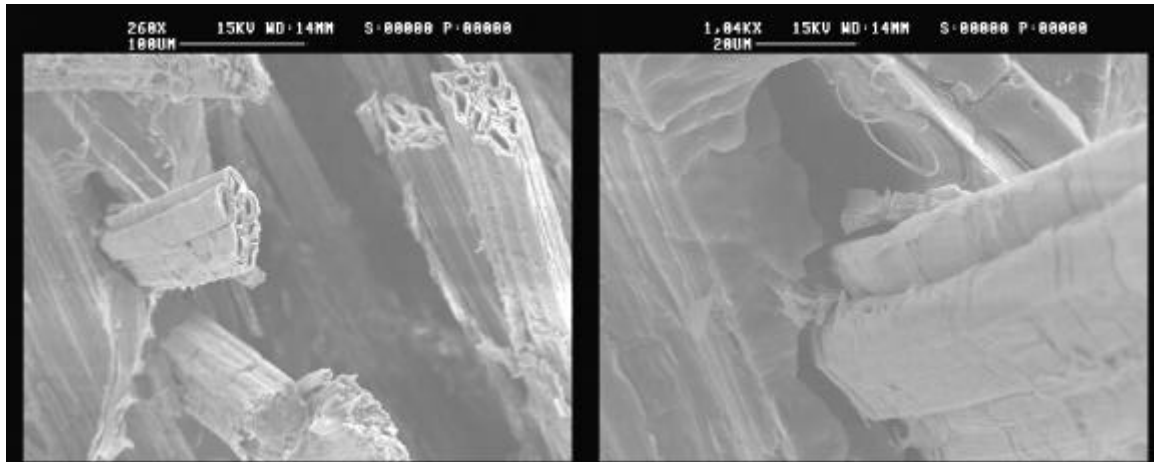


Fig. 6: SEM pictures of impact fracture surface of PHB/flax NMT composites.

### Injection moulding *versus* NMT

As shown in Figure 7, 8 and 9 there is no significant effect of processing method, i.e. injection moulding versus compression moulding (NMT), on the stiffness, strength and elongation of the composites. However, short-fibre-reinforced PHBV samples made through injection moulding showed clearly a lower impact resistance than NMT [Figure 10]. Compared to the long-fibre-reinforced NMT, injection moulded samples have much shorter fibres and hence less energy is absorbed by pull-out mechanisms. Similar to glass fibre systems, an increase in fibre length will particularly result in enhanced toughness. To study the effect of the compounding and subsequent injection moulding process on the initial fibre length of 10 mm the PHBV matrix was dissolved in chloroform and the fibre length distribution was measured.

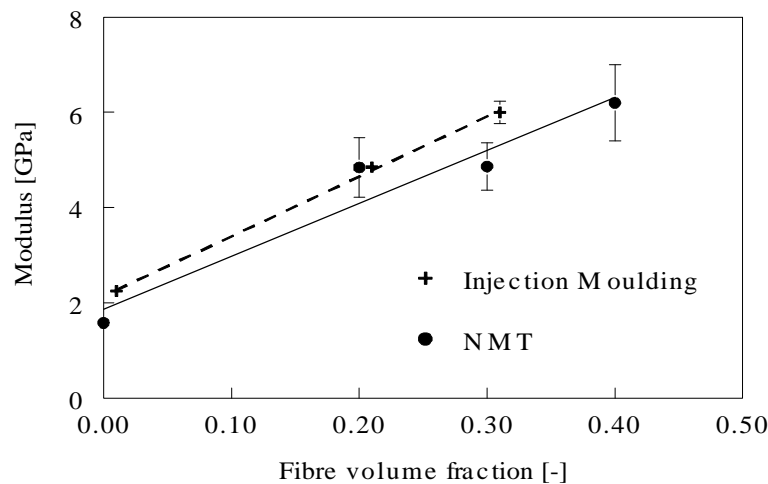
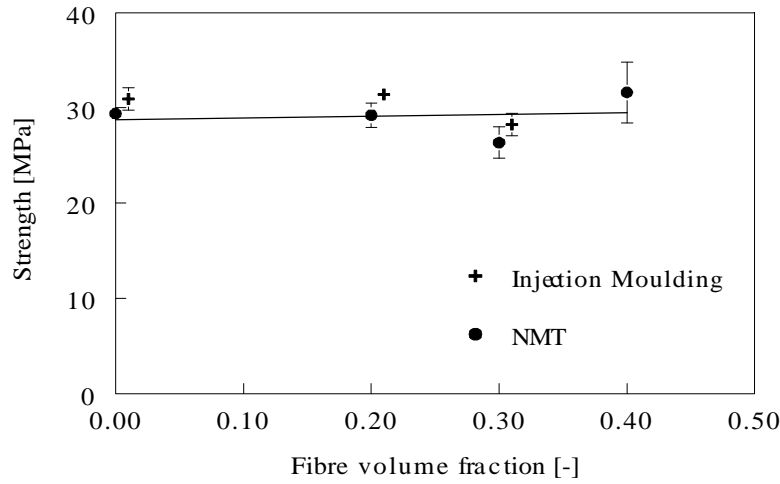
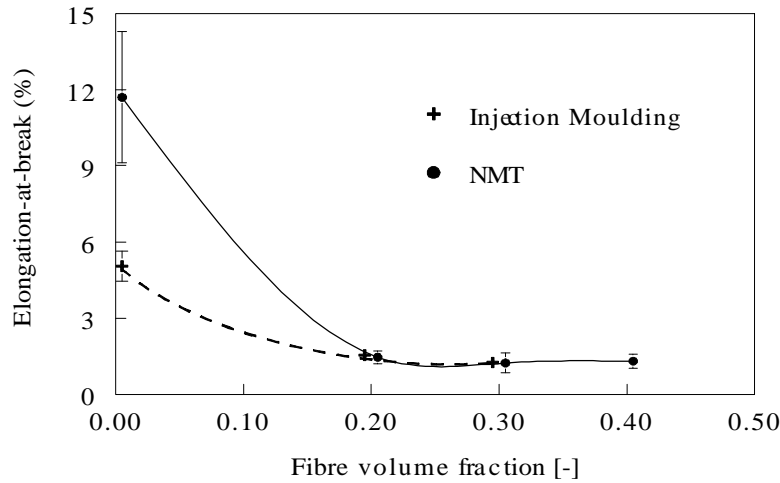


Fig. 7: Young's modulus of PHBV/flax as a function of fibre volume fraction and manufacturing method.



*Fig. 8: Tensile strength of PHBV/flax composites as a function of fibre volume fraction and manufacturing method.*



*Fig. 9: Elongation-at-break (%) of PHBV/flax composites as a function of fibre volume fraction and manufacturing method.*

Figure 11 shows a picture of the flax fibres after dissolving the PHBV matrix and Figure 12 gives the fibre length distribution. It was observed that the average fibre length, in the case of injection moulded sample, dropped from ~10 mm to ~1 mm, which lowers the impact resistance of the composites quite dramatically through reduced amount of fibre pull-out, especially when compared with long-fibre-reinforced NMTs. Although for many applications injection moulding of short-fibre-reinforced PHB/flax composites may seem the desired manufacturing method, there is a clear drop in composite toughness compared to the long-fibre-reinforced NMT.



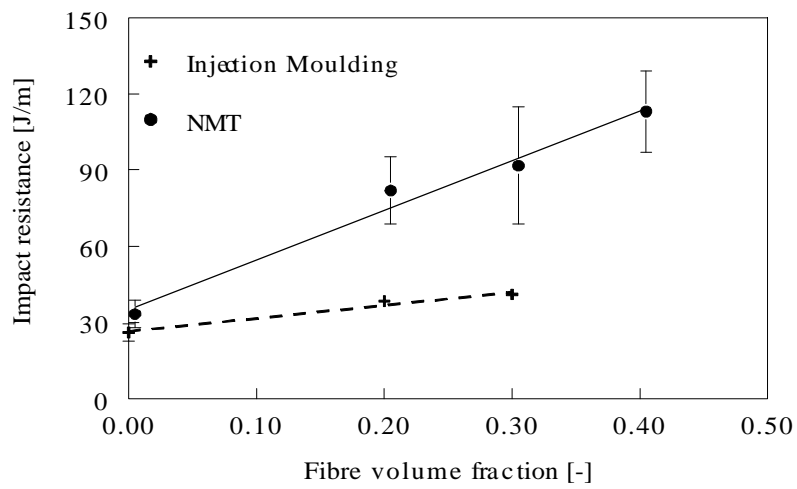


Fig. 10: Notched Izod impact resistance of PHBV/flax composites as a function of fibre volume fraction and manufacturing method.

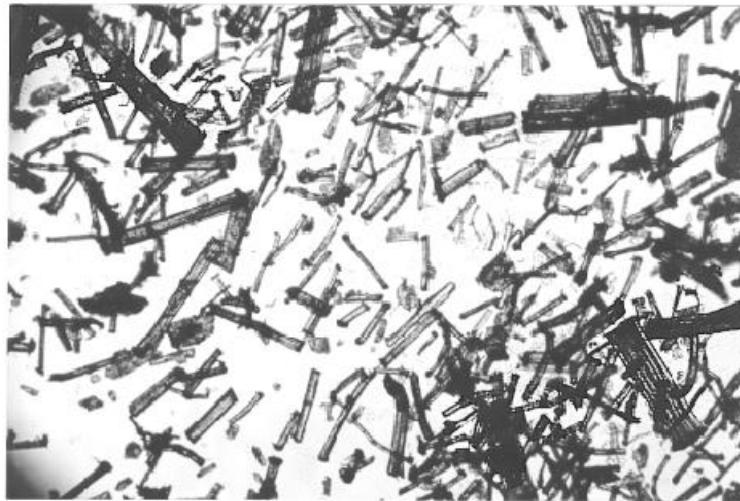


Fig. 11: Fibres left after dissolving the PHBV matrix in injection moulded sample.

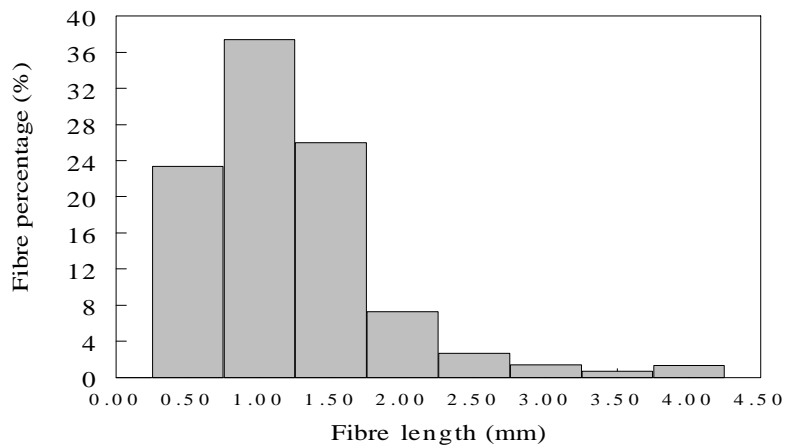


Fig. 12: Fibre length distribution in injection moulded sample.

## CONCLUSIONS

- Addition of cheap flax fibre to PHB can be advantageous as far as cost-performance of biopolymer composites is concerned and offers the chance to obtain cheaper products together with improved toughness, while retaining biodegradability of the resulting polymer composites.
- Strength of PHB- and PHBV/flax composites needs to be further optimised through modification of the fibre opening processes, yielding higher values for flax fibre strength and/or through the modification of the fibre-matrix interface.
- Short-fibre-reinforced PHBV/flax composites manufactured through injection moulding exhibit a stiffness and strength comparable to PHBV/flax NMT but a lower impact strength as a result of less energy absorption through pull-out.

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