Transcrystallisation in PP/flax composites and its effect on interfacial and mechanical properties

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Abstract The effect of flax fibre reinforcement on the crystallisation behaviour of polypropylene (PP) was investigated using a hot-stage polarising optical microscope. To follow the crystallisation kinetics, crystallisation temperature and time were varied. At crystallisation temperatures between 130 and 138 °C the most uniform and thickest transcrystalline layers were formed. The effect of transcrystallisation on the interfacial shear strength (IFSS) in micro-composites was studied by the fibre pull-out test method. It was found that the IFSS of the PP/flax system is slightly decreased with the presence of a transcrystalline interphase. Finally, the influence of the formation of a transcrystalline zone on the macromechanical properties of compression moulded PP/flax composites was studied.

Introduction

In recent years composites made of natural fibres have received considerable attention in literature and industry. Natural fibres are good candidates for reinforcing plastics because they are strong, lightweight, non-abrasive and relatively inexpensive [1–4]. Unlike man-made fibres, natural fibres are in fa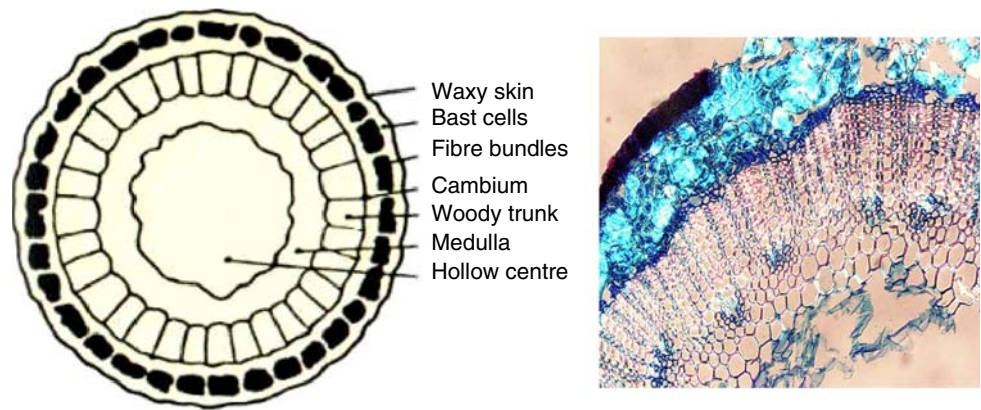ct composites by themselves. Flax fibres (Linum Usitatissimum) are a member of the family Linaceae that grow in moderate and moist climates. The principal chemical constituents of the flax fibre are cellulose, hemi-cellulose, lignin and pectin. As shown in Fig. 1, the fibres are located in the stalk of the flax plant. The fibres are covered by the bast, which is coated with a pectin skin. The long technical bast fibres isolated from the flax plant consist of cells or so-called elementary fibres (Fig. 2, [5]) with lengths generally around 2–4 cm and diameters in between 10 and 25 μm. The elementary fibres overlap over considerable length and are bonded together by pectin. Consequently, the elementary fibre cell wall is relatively thick, which accounts for the good mechanical properties of the fibre [6, 7]. To separate the bast fibres from bark and woody stem parts, the pectinous matter of the stem must be removed. The process of fibre separation through the action of dew, sun and fungi on the plants, spreading them thinly on the ground, is called dew retting. The fibre separation can also be done by purely mechanical means. Fibres obtained through the first method are called dew-retted flax and those obtained through the second method are called green flax. To reduce the moisture and rot sensitivity of flax fibres and to improve their reproducibility and quality, an upgrading method for flax was developed during the mid-1990s [8, 9]. This flax upgrading process does not use dew-retted flax as a feedstock, but uses the full rippled (deseeded) stalk, so-called straw-flax. The treatment consists of a steaming step of the rippled straw-flax at temperatures above 160 °C for approximately 30 min in an autoclave. This is followed by a drying step and a heating (curing) step above 150 °C for approximately two hours [8, 9]. After this treatment the fibres can be easily separated from the stem by a simple breaking and scutching process. The upgraded fibres are also known as Duralin® flax fibres. The use of flax fibres including upgraded flax fibres as
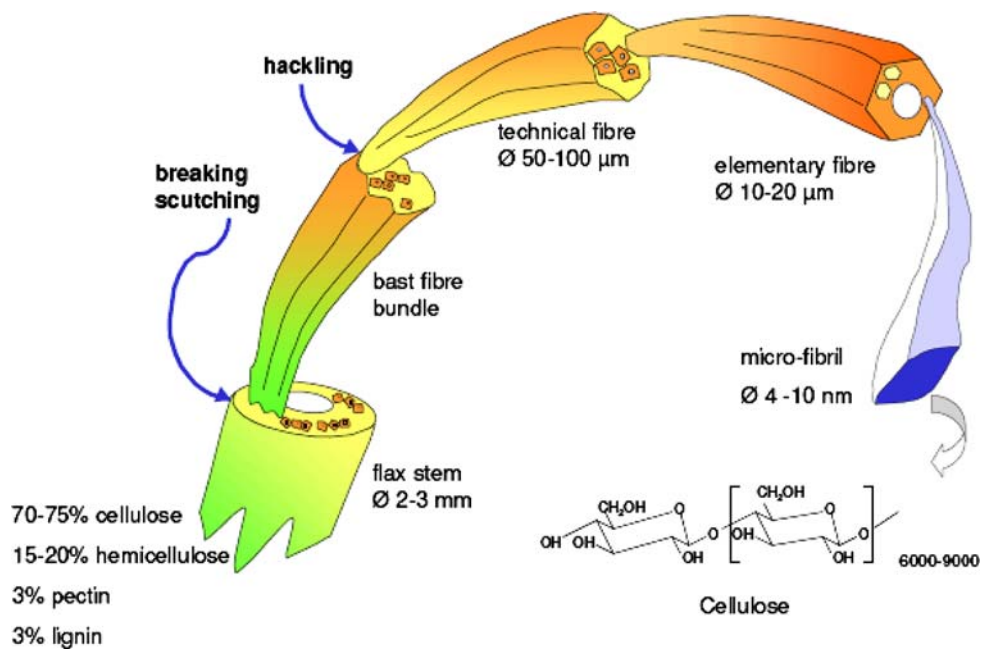
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Fig. 1 Schematic structure of the stem of a flax plant

- Waxy skin
- Bast cells
- Fibre bundles
- Cambium
- Woody trunk
- Medulla
- Hollow centre

Fig. 2 Composition of a flax fibre, showing its hierarchical composite-like structure [5]

hackling

breaking scutching

technical fibre
Ø 50-100 µm

elementary fibre
Ø 10-20 µm

bast fibre bundle

micro-fibril
Ø 4 -10 nm

flax stem
Ø 2-3 mm

70-75% cellulose

15-20% hemicellulose

3% pectin

3% lignin

Cellulose

reinforcement in PP was reported by Peijs and coworkers [6, 7, 10, 11] and Van den Oever et al. [5]. The effects of fibre loading, fibre length, orientation and interface compatibility by using a maleic adhydride-grafted polypropylene (MAPP) on the mechanical and environmental properties of the composites were studied.

Transcrystallisation

An important issue in the processing of semi-crystalline thermoplastic composites is the morphology of the matrix material. Morphological features such as degree of crystallinity, spherulite size, lamella thickness and crystalline orientation can all have a profound effect on the ultimate properties of the polymer matrix and hence on the composite. Crystallisation of a polymer from the melt can be divided into a two-stage process, namely nucleation and crystal growth. Two types of nucleation, namely homogeneous and heterogeneous can occur. Homogeneous

nucleation occurs as a result of random fluctuations of order in a supercooled phase. Heterogeneous nucleation occurs in the presence of foreign surfaces e.g. particles, fibres, impurities, dust or additives. In case of composites, when heterogeneous nucleation occurs with a sufficiently high density along a reinforcing fibre surface, the resulting crystal growth is restricted to the lateral direction so that a columnar layer develops around the fibre. This phenomenon is known as transcrystallisation [12–14]. Many factors have been reported to influence transcrystallisation including a shear induction on the fibre interface, axial thermal expansion coefficients of the fibre and polymer, an epitaxy between fibre and polymer, polymer molecular weight, fibre diameter and length, temperature gradients along the fibre, thermal conductivity of the fibre, topology and surface energy of the fibre, chemical composition of the fibre surface, crystalline morphology of the nucleating surface, crystallisation temperature and time and the sample cooling condition [15–30].

Effect of transcrystallinity on interfacial and macromechanical properties

Several studies have been conducted to observe the effect of a transcrystalline region on composite interfacial and macromechanical properties. From these studies it became clear that results regarding the effect of a transcrystalline interphase on the composite mechanical properties were quite contradictory [23, 28–39]. The existence of transcrystallinity has often been associated with an increase in interfacial properties through some kind of physical coupling between the fibre and polymer matrix [31]. As an example, Clark and Kander [32] found that a transcrystalline region in a reinforced Nylon-66 composite was responsible for the increase in interfacial shear strength (IFSS) as measured using a modified fibre pull-out test.

However, a number of authors did report no or even negative effects of transcrystalline interfaces on the interfacial properties of composites. For example, Heppenstall-Butler et al. [33] found no differences between IFSS values of differently processed iPP-Kevlar composites. Similarly, also Gati and Wagner [34] found that the presence of transcrystallinity produces little effect on the interfacial stress transfer capacity between PCL and Kevlar 149 by microbond or fibre pull-out test. For a carbon fibre/polycarbonate system, using a compressive fragmentation test, Wood and Marom [35] observed a reduction in the IFSS with the presence of a transcrystalline interphase. For PP/glass composites, Pompe and Mäder [36] suggested that large thermal stresses might build up during the transcrystallisation process, which in turn reduces the IFSS, whereas the increasing degree of crystallinity of the matrix material effectively decreased the mismatch in moduli between the fibre and matrix and thus enhancing the stress transfer efficiency across the interface. For the study in macrocomposite systems, Folkes and Hardwick reported that the generation of a transcrystalline interphase in PP/glass-laminated composite causes an increase in flexural strength and modulus [37, 38]. The formation of such transcrystalline layer was also shown to improve the mechanical properties of a short carbon fibre/PEEK composite studied by Zhang et al. [39].

However, for various cellulose fibre/PP composites, Son et al. found that the tensile strength of the macrocomposites decreases with the presence of a transcrystalline layer and also with increasing isothermal crystallisation time [23]. For the interfacial properties in microcomposites of dew retted and green flax/iPP systems, Zafeiropoulos et al. [28–30] reported that in the case of a single fibre fragmentation test the interfacial stress transfer was improved by the presence of a transcrystalline layer when compared to a system without the formation of a transcrystalline layer.

The aim of this study focuses on the effect of transcrystallinity on the interfacial and macromechanical properties of PP/flax systems. The effect of crystallisation temperature and time on the transcrystallisation behaviour of PP matrix is investigated. To follow the crystallisation kinetics, crystallisation temperature and time are varied. Transcrystallisation behaviour of PP/flax systems is observed by using a hot-stage polarised optical microscope. For the measurements of the interfacial properties, the fibre pull-out test is used in this study. This test is chosen because it is less sensitive to fibre or matrix defects when compared to a single fibre fragmentation test used by Zafeiropoulos et al. [28–30]. Particularly in the case of a natural fibre, which is basically an assembly of cells, each of finite length, the number of defects can be relatively large. These defects will inevitably influence the fragmentation process, hence leading to an overestimated value of the fibre-matrix interfacial strength [40]. The macromechanical properties of PP/flax composites were examined by tensile tests. The fracture surfaces of the macrocomposites were studied using environmental scanning electron microscopy (ESEM).

Experimental procedure

Materials

The upgraded Duralin® flax fibres used are long, continuous and chopped technical fibres, kindly provided by Ceres B·V. (Wageningen, The Netherlands). An isotactic polypropylene (iPP) matrix (XY6500T) with a melt flow index (MFI) of 35 in the form of pellets is supplied by Shell Co. Ltd.

Study of transcrystallisation behaviour

The effects of crystallisation temperature and time on transcrystallisation behaviour of iPP induced by flax fibres are observed under a hot-stage polarised light microscope. A small piece of matrix film is placed on a microscope slide, which is kept in a hot-stage, held at 210 °C until completely melted. A fibre is then placed onto the molten polymer and covered by another piece of matrix film. The system is left for 5 min to ensure complete melting of the polymer, after which the sample is cooled at controlled conditions.

Sample preparation for fibre pull-out test

Single flax fibres are selected from a bundle of flax fibres. Then, the fibres are inserted into capillaries and pierced-hole polymer films (using a needle) on the hot-stage (Fig. 3). The hole previously made on the polymer films is to ensure that
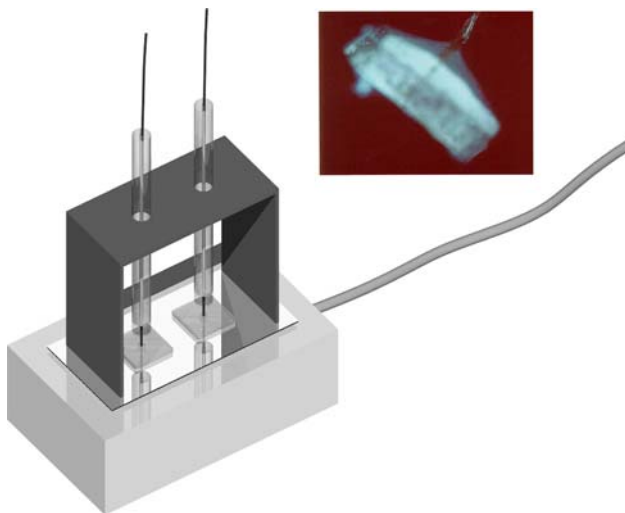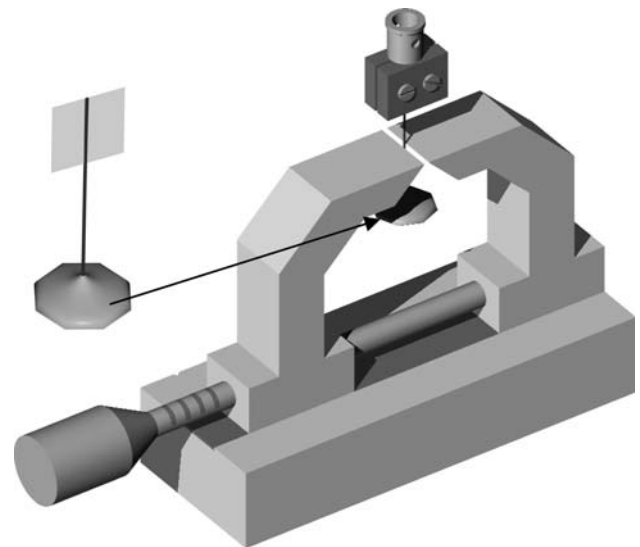
Fig. 3 Schematic representation of the set-up used for the preparation of flax fibre/PP pull-out sample and the prepared sample (at the corner)

Fig. 4 Schematic representation of the fibre pull-out test

the fibre remains straight and to facilitate the complete fibre insertion because the molten PP is very viscous and generally results in fibre breakage or bending when directly inserted. To get a range of embedded lengths, PP films with thickness between 0.2 and 1.3 mm are made using hot-pressing. When the fibre is pulled through the capillary and into the PP film the hot-stage is switched on and the heating starts. The hot-stage used is a Linkham Scientific LTS 350 with a Linkham TP 93 temperature controller unit. The hot-plate is heated to 210 °C and kept for 10 min, to melt all of the PP films around the fibre and to ensure that no residual stresses are present in the PP. To study the effect of transcrystallinity on the IFSS of the PP/flax systems, the specified cooling conditions as shown in Table 1 were used to prepare samples with the presence of an induced transcrystalline (TC) layer and other samples without the formation of a transcrystalline layer (TC free). An optical micrograph of the cross section of the prepared sample for the fibre pull-out test is given in Fig. 3 (inset).

Fibre pull-out test

The pull-out test consists of a single fibre embedded in a block of matrix. A monotonically increasing load is applied

to the fibre to pull it out of the matrix. A schematic representation of a pull-out sample is shown in Fig. 4. To measure the IFSS, a universal tensile tester (Frank type 81565) equipped with a load cell of 10 N is used. As shown in the schematic drawing, the sample is fixed in the upper clamp of the tensile testing machine, which is moved upward at a rate of 1 mm/min. A micrometer with sharp edged clamps, which is specially designed to obstruct the polymer bead from upward movement leading to fibre debonding or pull-out, is fixed in the lower clamp of the tensile testing machine.

After conducting the pull-out experiment the embedded fibre length (L_{em}) and fibre diameter are measured using an optical microscope. With the measured value of the maximum pull-out force the IFSS can be calculated by using Eq. 1 [41], where the assumption is made that the shear stress is uniformly distributed along the embedded length. The authors realise that this assumption is in fact invalid for the majority of this type of tests, as has been shown by numerous authors [e.g. 41–43], however, here Eq. 1 is merely used as a tool to compare data rather than to extract a true value for the interfacial shear strength.

$$\text{IFSS} = \frac{F}{A} = \frac{F}{\pi \cdot D_f \cdot L_{Em}} \tag{1}$$

Table 1 Cooling conditions used to prepare the PP/flax samples with (TC sample) and without (TC-free sample) the presence of induced TC formation. The interfacial shear strength (IFSS) of the samples examined by the fibre pull-out test is calculated and also given

Sample	Cooling steps	IFSS (MPa)
TC	Cooling from 210 to 130 °C at 10°C/min → Crystallisation at 130 °C for 10 min → Quench to RT	7.8
TC-free	210 °C-RT (quench to room temperature, RT)	9.8

in which

> IFSS = Interfacial shear strength (N/mm^2)
> F = Maximum pull-out force (N)
> D_f = Average fibre diameter (mm)
> L_{em} = Embedded length (mm)
> A = Embedded area (mm^2)

Preparation of macrocomposites

To study the effect of transcrystallinity on the mechanical properties of macrocomposites, samples are made by compression moulding of chopped PP/flax compound. Compounding of chopped flax fibres (10 mm length and 20 vol%) and PP is carried out in a Brabender kneader (HBI system 90) at a temperature of 210 °C and at a rotor speed of 30 rpm for 30 min. Then, the mixed compound is compression moulded in a hot-press at a temperature of 210 °C, followed by cooling at the specified conditions as shown in Table 1.

Characterisation of macrocomposites

A microtomed slice of the macrocomposite is prepared and investigated under a polarised optical microscope. Uniaxial tensile tests on random short flax fibre reinforced PP composites are performed in a Frank tensile testing machine

(model 81565) according to ASTM D638. An extensometer is used to monitor the elongation of the specimen during testing. The fracture surfaces of the composites were studied using environmental scanning electron microscopy (Philips ESEM-XL series).

Results and discussion

Influence of crystallisation temperature and time on transcrystallisation behaviour

After isothermal crystallisation from the melt a transcrystalline (TC) layer was found having lamellar crystals grown perpendicular to the fibre axis. The formation of such a TC interphase around a flax fibre in PP matrix at different crystallisation temperatures is shown in Fig. 5. At crystallisation temperatures of 130 and 138 °C (Fig. 5b and c, respectively), the most uniform and thickest TC layers are obtained. Clearly, the nucleation density on the fibre surface is higher than in the bulk matrix at these conditions. Therefore, the growth of nucleated transcrystals can be increased because of less competition from spherulitic nucleation in the polymer melt, which leads to more space being available in the bulk matrix. As a result, the TC layers grow more uniform and further before they impinge with spherulites in the bulk matrix. At lower crystallisation temperature, 125 °C

Fig. 5 Effect of crystallisation temperature on transcrystallisation behaviour of PP/flax system. **a** 125 °C. **b** 130 °C. **c** 138 °C. **d** 140 °C. The pictures were captured at a cooling time of 10 min and a cooling rate of 10 °C/min. The scale bar, 1 cm = 53 μm
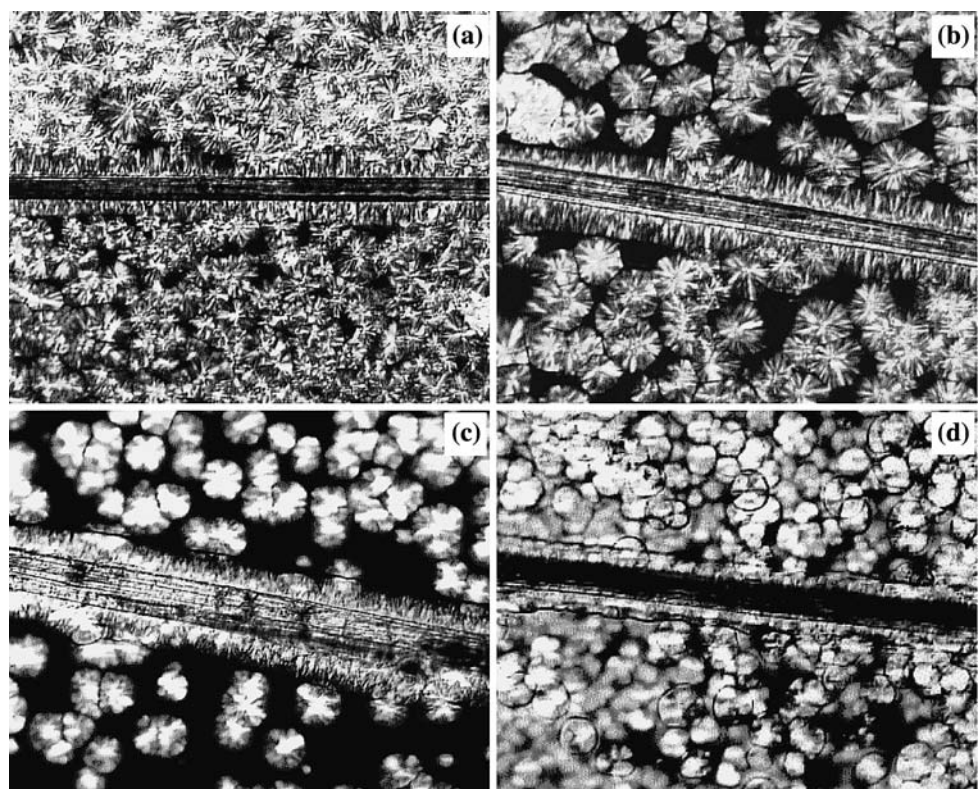
(Fig. 5a), a slightly thinner and less uniform TC layer is observed. With increasing supercooling, as expected the number of nuclei increases noticeably in the bulk matrix [15]. Thus, the TC layer cannot grow far before it impinges with the numerous spherulites formed in the bulk matrix. On the other hand, at high crystallisation temperature, 140 °C, the nuclei density on the fibre surface decreases, and therefore, the formation of the TC layer is slower [15]. Consequently, a TC layer is observed with a number of spherulites formed in the melt as illustrated in Fig. 5d. The maximum crystallisation temperature for the PP/flax system studied is 140 °C. At higher crystallisation temperatures, no TC formation is observed, i.e. crystal growth occurs only in the bulk matrix and not on the fibre surface.

Figure 6 shows the TC zone grown around the flax fibre in a PP matrix at a constant crystallisation temperature of 138 °C with increasing crystallisation time. It is clear that the thickness of the TC layer or interphase increases with time and reaches a maximum value after a certain time. The measured value of TC thickness plotted versus time is shown in Fig. 7.

Influence of transcrystallinity on interfacial properties

Two different conditions, quench and slow cooling (as shown in Table 1), are used to prepare the samples for the fibre pull-out tests to investigate the effect of transcrystallinity on the IFSS of the PP/flax system. The observation under the polarised optical microscope of flax in PP matrix for both conditions is shown in Fig. 8. After the quench cooling, no TC layer is found to be formed at the fibre surface (TC-free sample, Fig. 8a), whereas, in the case of

Fig. 6 Effect of crystallisation time on transcrystalline thickness in PP/flax system at a crystallisation temperature of 138 °C. Cooling rate 10 °C/min. **a** 2 min. **b** 6 min. **c** 10 min. **d** 18 min. **e** 24 min. **f** 34 min. The scale bar, 1 cm = 35 μm
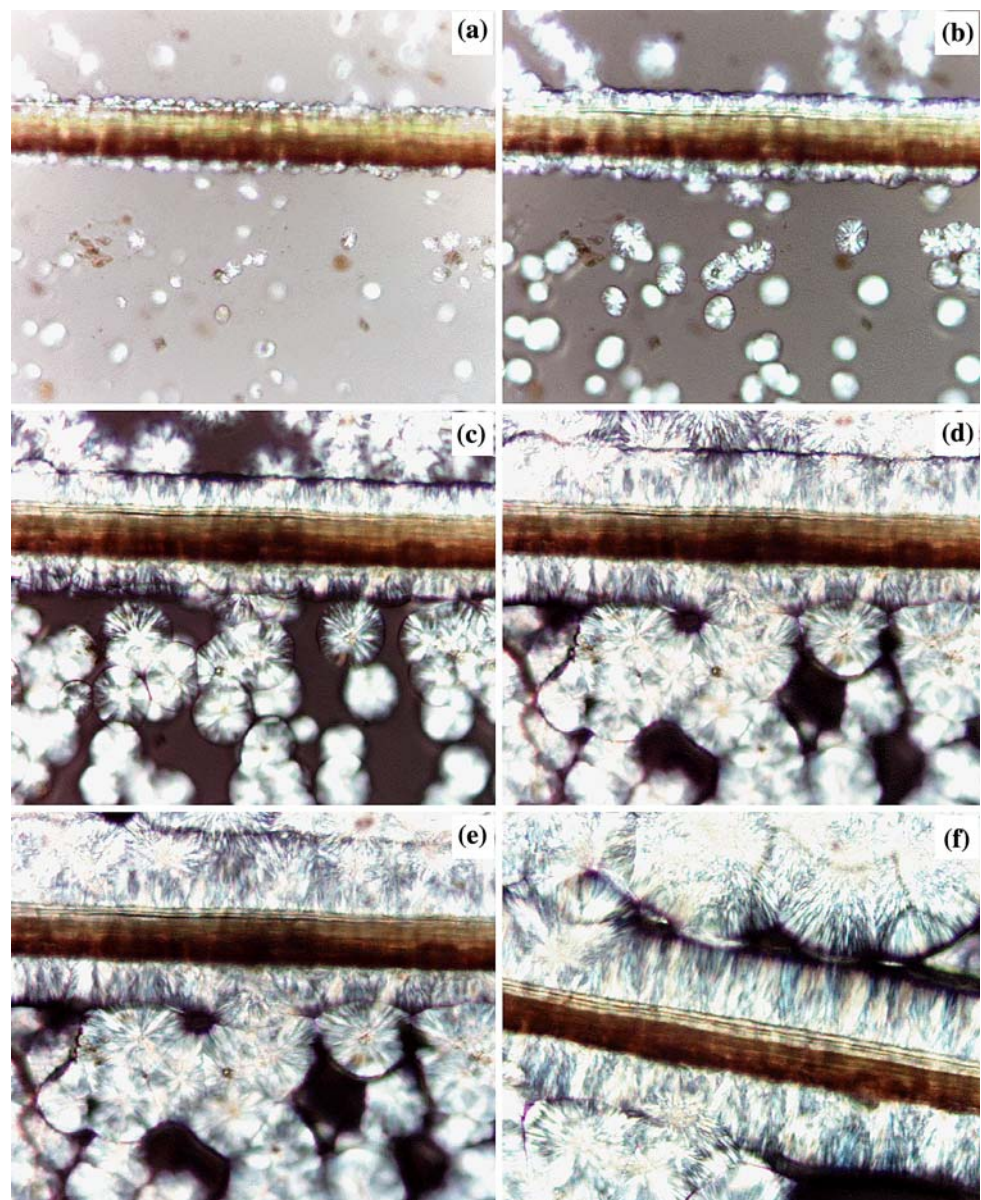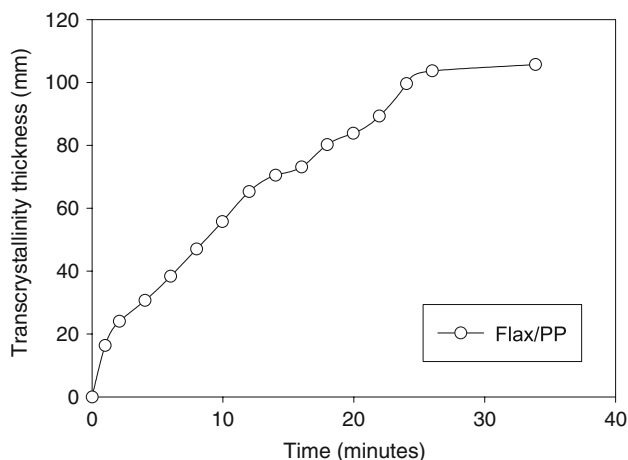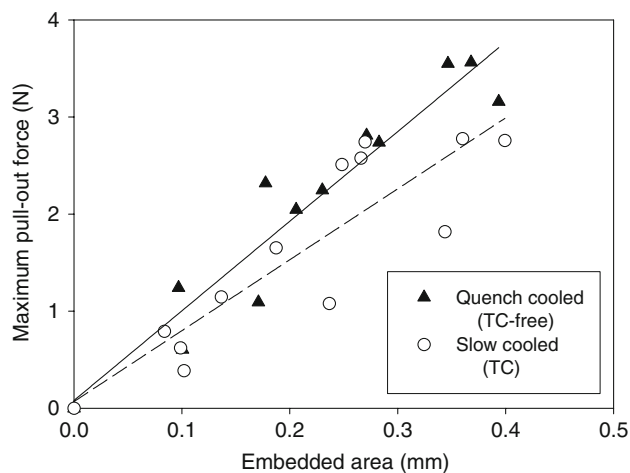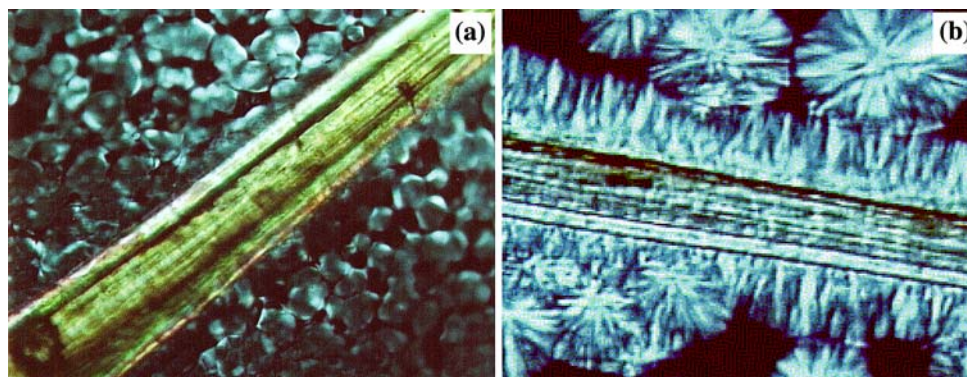
Fig. 7 Development of transcrystalline thickness with time around flax, cooled from 210 °C to crystallisation temperatures of 138 °C at a cooling rate of 10 °C/min

Fig. 9 Maximum pull-out force vs. embedded area for (▲) quench cooled sample (TC-free) and (○) slowly cooled samples (with the presence of TC)

slow cooling, an induced TC layer is formed around the fibre (TC sample, Fig. 8b). From the fibre pull-out tests for both samples, the maximum pull-out forces are plotted as a function of the embedded area (shown in Fig. 9). Embedded area is selected instead of embedded length, as often used for such studies, because natural fibres generally do not have a constant diameter and therefore do not allow for comparison of the data. The IFSS of PP/flax samples are calculated by Eq. 1 and shown in Table 1. These values compare very well with other data reported for PP-based systems. For example, IFSS values of 7.8 and 12.4 MPa have been reported by Mäder et al. [44] for glass fibre/PP systems without and with a compatibiliser based on maleic-adhydride grafted polypropylene. For the TC-free PP/flax sample in the present work, without adding any coupling agent, an average IFSS of 9.8 MPa is measured. This relatively high IFSS compared to PP/glass is probably due to the rougher surface of the natural fibres, which can result in additional physical coupling between fibre and matrix. However, the results also show that the presence of a TC layer negatively affects the IFSS of the PP/flax system, reducing the stress transfer capability from the matrix to the fibre.

These findings are in contrast to those reported for a dew-retted flax/PP system by Zafeiropoulos et al. [28]. They reported IFSS values of 12 and 23 MPa for samples without and with a TC layer, respectively, and as such found that the formation of a TC layer had a positive effect on the interface properties. Although this difference could be partly caused by differences in the type of flax, PP, sample processing and data reduction, the main difference is most likely due to the very different micromechanical tests used. The IFSS values reported by Zafeiropoulos et al. are also much higher than the values quoted in this work, i.e. 23 MPa for the sample with a TC layer, compared to 7.8 MPa in the current work. These high values could be due to an overestimation of the IFSS calculated from their single fibre fragmentation test. In the case of a natural fibre, which is an assembly of cells of finite length, the number of defects at each overlap between cells can be relatively large. Hence, the failure process will most likely be influenced, if not dominated, by these regular defects, inevitably influencing the statistical fragmentation process as it occurs in man-made fibres [14, 40, 41]. This can lead to shorter fibre fragments and an overestimation of the

Fig. 8 Pictures of flax in PP (**a**) quench cooled from 210 °C (TC-free sample) and (**b**) slow cooled from 210 °C to 130 °C at 10 °C/min followed by isothermal heating at 130 °C for 10 min and then further quenched to room temperature (TC sample)

IFSS. Besides fibre defects, in the case of Zafeiropoulos et al., the fibre fragmentation process seemed also to be influenced by matrix cracking. In their work, on many occasions the location of a fibre break coincides with crazes or cracks within the TC layer, located at the boundaries between the transcrystals. This damage consisting of an interlamellar crack within the TC zone, which has also been observed in PP/glass systems [31], eventually propagated through the fibre [28]. Clearly, such a matrix cracking-induced fibre failure process will make the fragmentation test invalid. The pull-out test, because of its short embedded lengths, is clearly less sensitive to such fibre and matrix defects and therefore possibly a more reliable micromechanical test for transcrystalline matrix systems incorporating natural fibres.

Influence of transcrystallinity on macromechanical properties

To investigate the effect of transcrystallinity on the macromechanical properties of the PP/flax composites, the same two different cooling conditions (quench and slow, Table 1) are used to prepare bulk composite samples. So far, in bulk composites, a clear induced transcrystallisation of PP on flax fibres has not been reported. In the present work the formation of TC interphases in a bulk composite system is being attempted. Figure 10 shows a picture of a microtomed slice of the slowly cooled PP/flax composite sample observed under a polarised optical light microscope. The picture clearly shows the presence of a TC interphase around flax fibre as indicated by the white arrow. The white spots in the middle are a group of elementary fibres or technical fibre (see Fig. 2). However, the TC formation is only partial and not symmetrical around

the fibre. Incomplete wetting of PP which leads to a decrease in the nucleation ability of the fibre could be one of the reasons causing this unsymmetrical growth of such a TC layer [22].

From mechanical tests, it is observed that PP/flax composites have a lower modulus and strength with the presence of TC interphase (Fig. 11). There are two main reasons for this. Firstly, the influence of the inferior interfacial properties of this system as previously shown through the pull-out tests (TC sample, Table 1 and Fig. 9). Secondly, the different morphology of the PP matrix itself in composites processed using different cooling conditions (fast quench cooled versus slowly cooled). As shown in Fig. 8, the quench cooled sample has relatively small spherulites formed because the PP molecules do not get enough time to crystallise and grow during quenching. In the slowly cooled sample, relatively large spherulites can be seen (as well as transcrystals). However, the impingement of two spherulite or crystalline fronts will result in a weak fracture path due to the lack of tie-chains between them [38]. Therefore, this might easily lead to crack initiation and, consequently, brittle failure of the composite. This hypothesis is well supported by the ESEM results. As shown in Fig. 12a, the fracture surface of the slowly cooled composite shows a granular surface morphology which indicates the brittle nature of the fracture unlike the quench cooled composite (Fig. 12b). The latter has a higher tie-chain density between crystals leading to improved stress transfer and subsequently better mechanical properties of the composite [23].

Although not the subject of the current study, it would have been interesting to study the kinetics of transcrystallisation of isotactic polypropylene on flax fibres in more detail. Transcrystallisation of iPP in the presence of fibres can result in different crystalline polymorphs. Although it is expected that for our iPP/flax system transcrysallisation is of α (monoclinic) structure, β (hexagonal) TC layers
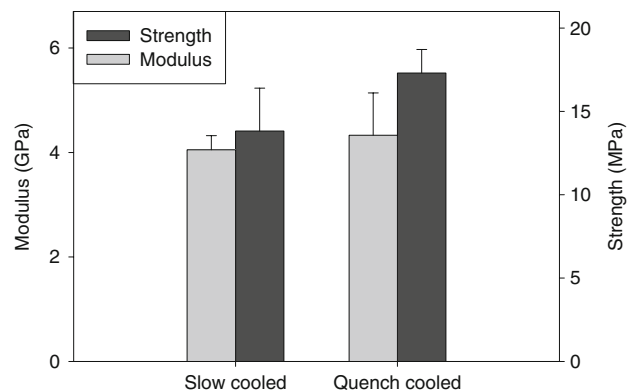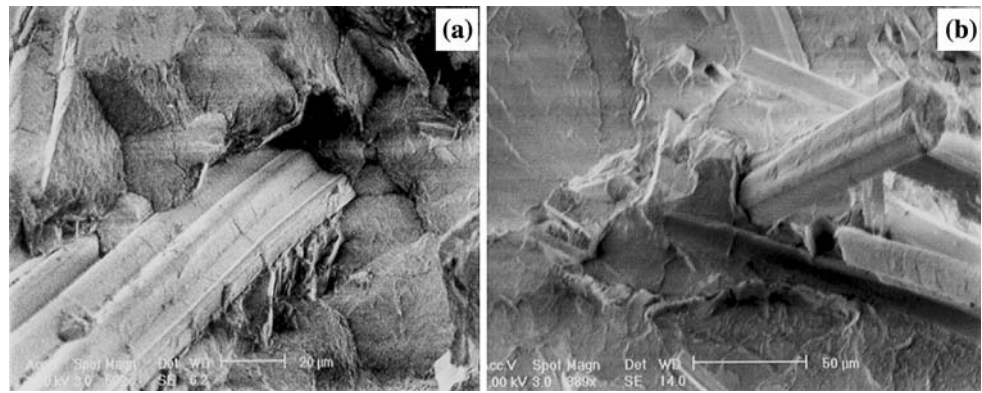

Fig. 10 Polarised optical microscopy picture of a microtomed cross section of the slowly cooled PP/flax composite sample, cut perpendicular to the fibre axis, showing the presence of a non-symmetrical transcrystalline layer developed around the fibre

Fig. 11 Effect of crystallinity condition on tensile modulus and strength of bulk PP/flax composites

would be possible especially if they were generated through exerting some kind of shearing stress. The γ (orthorhombic) TC is less likely since it is obtained under high pressure [45–47].

transfer, differences in bulk PP matrix morphology due to the different cooling conditions (quench versus slow) can be the reason for the reduction in mechanical properties of the bulk composites with a TC interphase.

Conclusions

Flax fibres are good nucleating agents for PP matrix leading to the development of a well-defined TC interphase zone. Within the range of optimum crystallisation temperatures for PP, i.e. 130–138 °C, the nucleation density on the fibre surface is higher than in the bulk matrix; hence, there is less competition from spherulitic nucleation and growth in the polymer melt. Therefore, TC layers can grow further, becoming thicker and more uniform, before they impinge with spherulites grown in the bulk matrix. At a constant crystallisation temperature, the thickness of the TC interphase increases with time and reaches a maximum value after a certain time. From fibre pull-out tests it was found that the presence of TC layers negatively affects the interfacial properties of the PP/flax system. These results are in contradiction with previous work by Zafeiropoulos et al. [28]. They evaluated the effect of TC on the interfacial properties of PP/flax using fibre fragmentation tests, and reported a positive effect of a TC interphase on interface properties. These differences can be caused by the different micromechanical tests used and the sensitivity of the fibre fragmentation test to regular fibre and matrix defects that can overrule the statistical fibre breakage process, resulting in shorter fragment lengths and an overestimation of the IFSS. Therefore, because of its relative insensitivity to fibre and matrix defects, the pull-out test—with all its limitations—is probably the more reliable micromechanical test method for the evaluation of fibre-matrix adhesion in TC matrices based on natural fibres.

Also in real bulk composites, the PP/flax composite with an induced TC interphase exhibited a lower modulus and tensile strength than the one without a TC interphase. However, besides the influence of inferior interfacial stress

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