

LIQUID MOULDING OF TEXTILE REINFORCED THERMOPLASTICS

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ABSTRACT

The high viscosity of thermoplastic matrices hampers fibre impregnation. This problem can be overcome by using low viscous polymeric precursors such as cyclic butylene terephthalate (CBT[®] resins), which polymerise to form a thermoplastic matrix. This allows thermoset production techniques, like Resin Transfer Moulding (RTM), to be used for the production of textile reinforced thermoplastics. The mechanical properties of the resulting composites indicated a brittle matrix, which led to a more detailed investigation of the matrix properties. Due to the processing route inherent to the RTM process, the crystallites of the matrix consisted out of well-defined, thick and well-oriented crystal lamellae. Together with a low density of tie molecules, these large and perfect crystals cause polymer brittleness. Although not a valid option for the RTM production route, crystallisation from a truly random melt and at a sufficiently high cooling rate would substantially improve the ductility.

1 INTRODUCTION

The production of textile reinforced thermoplastics is not as straightforward as for their thermoset counterparts. The high melt viscosity of thermoplastics, which is two orders of magnitude higher than the viscosity of thermoset precursors, complicates the impregnation of the textile preform. Thermoplastics however have some advantages over thermosets, namely a higher toughness and the possibility to melt and hence post-shape and recycle them. There are two main routes to impregnate a textile with a thermoplastic matrix [1]. The first route consists of reducing the distance that the resin is required to flow, like in commingled yarns. The other possibility is a substantial viscosity reduction, which allows thermoset production routes, like liquid moulding, to be used.

Recently, more attention has been paid to infusing low viscous thermoplastic prepolymers, which are subsequently polymerised, into a fibre preform to form the final part, [2-5]. Due to the processing route followed, matrix properties can differ from their classically produced counterparts. This paper reports on the properties of glass fibre reinforced polybutylene terephthalate produced by resin transfer moulding as well as on the properties of the matrix system used.

2 MATERIALS AND METHODS

2.1 Materials

The prepolymers used in this study were the cyclic butylene terephthalate oligomers (CBT[®] resin) supplied by Cyclics Corporation. These oligomers are precursors for the thermoplastic polybutylene terephthalate (PBT). The number of butyl groups in the oligomer mixture varies from two to seven, resulting in a melting range from 130-160 °C. Before processing, the oligomers were dried overnight at 110 °C to remove residual moisture, which could interfere with the polymerisation reaction. The tin-based transesterification catalyst (Fascat[™] 4101) is commercially available from Atofina Chemicals Incorporated.

The reinforcements used were two mainly unidirectional, non-crimp glass fibre fabrics, which were also dried overnight at 110 °C before processing. The first non-crimp fabric (S-UD)

supplied by Saertex Wagener GmbH has a total areal density of 951 g/m². Although this fabric is mostly unidirectional, a small amount of 90° fibres (27 g/m²) was added to ensure for fabric stability. Three layers of this fabric were used, resulting in a total fibre volume fraction of 54 % for a composite thickness of 2 mm.

Ahlstrom supplied the second type of non-crimp fabric (A-UD), which consists out of three levels, 0°, 90° and a random mat. The areal density of these individual levels was determined experimentally resulting in respectively 1217, 60 and 53 g/m². Two layers of this fabric were used (0, R, 90)_s to reach a fibre volume fraction of 52 % for a 2 mm thick composite.

Injection moulded plates (6 × 6 × 2 mm³) of commercially available PBT, namely Ultradur B4500, were supplied by BASF-AG as a reference material. This material will be simply referred to as PBT.

2.2 Production process

The production of glass fibre reinforced polymerised CBT (GF-pCBT) closely resembles the well-known RTM process for thermoset composites. The oligomers are heated to a temperature (190 °C) above their melting point, after which the catalyst (0.45 wt%) is added. The resulting mixture is stirred for a well-defined time (15 s), before it is vacuum infused into the closed mould, containing the fibrous reinforcement. During this stirring time, polymerisation already starts, resulting in a continuously increasing viscosity and thus a limited time window for mould filling. Once the mould is completely filled, in- and outlet ports are closed after which sufficient time (30 min) should be available to complete the polymerisation reaction and crystallisation (at the polymerisation temperature). Flat plates (320 × 200 × 2 mm³) of both unreinforced pCBT and GF-pCBT were successfully produced.

2.3 Reprocessing

A lab-scale injection moulding machine was used to produce tensile bars, starting from both the grinded pCBT and PBT. The melt temperature was around 250 °C whereas the mould was kept at room temperature.

2.4 Measurement techniques

Gel Permeation Chromatography (GPC): The measurements were performed with a mixture of chloroform/hexafluoro-2-propanol (HFIP) as solvent (98/2 CHCl₃/HFIP). The flow rate was 0.8 ml/min at a temperature of 20°C. Two Waters PL HFIPgel columns were used in series. The chromatograph was connected to Waters 484 UV detector working at 254 nm. In order to relate retention time to molecular weight, a universal calibration was made using various polystyrene standards. For sample preparation, approximately 2 mg of matrix was dissolved in 80 µl of HFIP. After total dissolution, the solution was diluted by 4 ml of chloroform.

The degree of conversion was determined from these GPC measurements by comparing the amount of remaining oligomers to the amount of polymer and is calculated according to Eq. (1).

$$\alpha = 1 - \frac{A_{oli}}{A_{tot}} \quad (1)$$

with A_{oli} the area under the oligomer peaks of the retention time curve and A_{tot} the total area under the retention time curve.

Differential Scanning Calorimetry (DSC): In order to determine the degree of crystallinity, defined in Eq. (2), melting endotherms were recorded at 10 °C/min.

$$\chi_{c(wt\%)} = \frac{\Delta H_m}{\Delta H_\infty} \quad (2)$$

where ΔH_m is the melting enthalpy of the polymer, and ΔH_∞ is the melting enthalpy of the fully perfect crystal of PBT, which is found in literature to be 142 J/g [6].

Wide Angle X-ray Diffraction (WAXD): Diffraction patterns were obtained in reflection mode with a Siemens D500 goniometer. All experiments used Cu K α radiation (40 kV-40 mA) and the angular range for the WAXD is $5^\circ < \theta < 50^\circ$.

Transmission Electron Microscopy (TEM): First, the sample surfaces were prepared for contrast colouring. Then the samples were stained with ruthenium tetroxide by exposing them for 48 hours to a RuCl₃ × NaClO vapour after which they were cut for the first time with a diamond knife. The staining procedure was repeated before recutting the samples and depositing them on a TEM grid. TEM micrographs were obtained on a LEO 922 transmission electron microscope operating at 200 kV.

Mechanical properties: The unidirectional composites as well as the pCBT are tested in three point bending according to ASTM D790-84. The moduli of the composites were compared to the theoretical properties, calculated according to the classical laminate theory. Small injection moulded tensile bars were used for tensile testing of the injection moulded pCBT (IM-pCBT) and PBT (IM-PBT).

3 RESULTS AND DISCUSSION

3.1 Mechanical properties of composites

Table 1 shows the flexural properties of the glass fibre reinforced pCBT. The calculated theoretical moduli compare well to the experimental values, both in longitudinal and transverse direction.

Table 1 Flexural properties of GF-pCBT

	E_{11} (GPa) [calc]	E_{22} (GPa) [calc]	σ_{11} (MPa)	σ_{22} (MPa)
S-UD	38.3 ± 1.2 [39.4]	8.7 ± 0.9 [10.0]	766 ± 113	66 ± 6
A-UD	37.8 ± 1.4 [38.8]	6.8 ± 1.8 [8.0]	901 ± 64	96 ± 4

Fig. 1 shows the stress-strain behaviour of the S-UD reinforced pCBT. Due to the nature of the fabric, containing not only 0° but also a small amount of 90° oriented fibres, this measured strength is actually an overestimation of the real transverse strength. The knee in this curve indicates failure of the outer layer, which does not induce total failure due to the ‘cross-ply’

nature of the specimen. Compared to the flexural strength of PBT, which is known to be in the range of 80-115 MPa [7], the real transverse strength is however quite low.

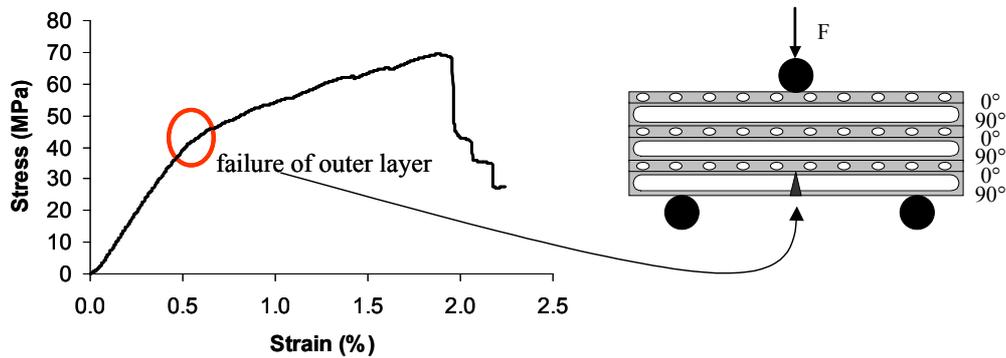


Fig. 1 Stress-strain curve of transverse flexural test of S-UD reinforced pCBT

The transverse strength is a non-fibre dominated property and hence influenced by both the matrix and interface properties. In glass fibre composites, large local stress concentrations around the fibres exist, causing cracks normal to the loading direction either at the matrix-fibre interface or in the matrix [8]. These stress concentrations are responsible for lowering the transverse strength of thermoset composites below the strength of the matrix. Thermoplastic matrices on the other hand should be able to compensate for these stress concentrations by local plastic deformation of the matrix.

A low transverse strength is therefore an indication of either poor fibre-matrix interface properties or matrix brittleness. Glass fibre reinforced pCBT prepared with commercially available “epoxy-compatible” sized fibres should have adequate interface properties. Bahr [9] showed that compared to composites made from unsized glass fibres, the interlaminar shear strength improved substantially (63 versus 24 MPa). Compared to glass fibre reinforced epoxy on the other hand, the ILSS was somewhat lower but the pCBT samples did show some yielding.

Unidirectional composites manufactured by vacuum bagging have shown a transverse strength close to the tensile strength of PBT [10], indicating both adequate interface properties and plastic deformation of the matrix. These vacuum bagged composites were however produced differently compared to the RTM samples (lower catalyst level, different cure profile). The importance of the processing route on the transverse properties of composites has been discussed previously for glass fibre reinforced polyamides [11, 12] and was related to the crystalline nature of the matrix. Therefore, the properties of pCBT are investigated in order to assess the possible brittleness of pCBT as produced in RTM.

3.2 Characterisation of matrix

In order to assess the properties of pCBT, flexural tests were performed on both pCBT, manufactured as it would be in RTM, and classically produced PBT. The results are shown in Table 2. It is clear that the pCBT behaves differently from PBT. Apart from the higher modulus, pCBT breaks in a brittle manner whereas the PBT samples do not break at all, but show a yield point.

Table 2 Flexural properties of pCBT compared to PBT

	E (MPa)	σ^* (MPa)^a	ϵ^* (%)^a
pCBT < T_m^b	3.2 ± 0.1	58 ± 2	1.8 ± 0.1
pCBT > T_m^c	3.1 ± 0.2	73 ± 14	2.3 ± 0.7
PBT	2.2 ± 0.1	73 ± 11	5.3 ± 0.3

^a stress and strain at break for pCBT, stress and strain at yield for PBT

^b CBT polymerised below the melting point of PBT

^c CBT polymerised above the melting point of PBT

There are a number of reasons why a thermoplastic polymer can be brittle. Apart from defects and impurities, a low molecular weight, a high degree of crystallinity, very large spherulites or a low density of (intercrystalline) tie molecules can substantially reduce ductility.

Table 3 shows the results of the GPC and DSC measurements. Although the molecular weight of PBT is somewhat higher than that of pCBT, both exceed the critical molecular weight of 50 kg/mol [13]. The molecular weight can therefore not be responsible for the brittle behaviour of pCBT. The DSC measurements on the other hand show a significant difference in the degree of crystallinity of pCBT and PBT, which concurs with the higher modulus. This elevated degree of crystallinity of pCBT however cannot (solely) explain the large decrease in ductility since PBT with even higher degrees of crystallinity and of comparable molecular weight do exhibit ductile behaviour [13].

Table 3 Properties of pCBT compared to PBT

	M_n (kg/mol)	M_w (kg/mol)	α (%)	χ_c (%)
pCBT < T_m	29.3 ± 0.2	61.4 ± 0.5	98.2 ± 0.1	34 ± 2
pCBT > T_m	35.0 ± 0.4	73.3 ± 0.6	98.7 ± 0.1	27 ± 2
PBT	33.8 ± 0.4	69.3 ± 0.2	98.8 ± 0.1	24 ± 1

The production of PBT and pCBT is completely different. The PBT samples are injection moulded from fully polymerised PBT pellets, therefore rapidly crystallised from the melt. The pCBT on the other hand is produced from cyclic oligomers, below the melting point of the resulting polymer (pCBT < T_m). Due to the polymerisation below the melting point of pCBT, crystallisation can start before the completion of polymerisation. According to Wunderlich [14], this simultaneous polymerisation and crystallisation can lead to a very different crystal morphology ranging from a fully extended chain conformation to a folded chain conformation, which is the typical conformation for crystallisation from the melt.

The tie molecule density can also be influenced by simultaneous polymerisation and crystallisation. Miller [13] stated that if oligomers are added to polymer chains that already began to crystallise, only short amorphous segments are attached to crystal growth fronts, which in turn have a low probability of becoming part of more than one lamellae and thus

forming tie molecules. Moreover, the transesterification catalyst remaining in the polymer can also influence the amount of tie molecules. Indeed, the catalyst molecules cannot be included into the polymer crystal, but probably concentrate at the surface of the growing crystals. Owing to the mechanical tensions arising from packing density differences at the crystal boundaries, such a local transesterification enhancement would drastically decrease the amount of tie molecules.

Consecutive or simultaneous polymerisation and crystallisation should have a large effect on both the crystal conformation and the tie molecule density. Therefore, pCBT plates were produced as described above but at a temperature exceeding the melting point of PBT ($pCBT > T_m$), i.e. 230 °C. Since isothermal production is impossible at this temperature, the mould was first cooled down to 190 °C and kept there for 30 minutes before cooling down to room temperature. The mechanical and physical properties of these plates are also shown in Table 2 and Table 3. Although these samples were produced with consecutive polymerisation and crystallisation, they still exhibit a brittle behaviour.

It is known that the cooling rate and crystallisation temperature of PBT have a significant effect on the crystal structure and properties of PBT. Slower cooling produces a higher crystallinity, usual type spherulites and greater rigidity in the polymer [15]. The greater rigidity can partially be ascribed to the increased crystallinity. Therefore, the brittleness of pCBT crystallised from the melt can be (partly) attributed to the slow crystallisation kinetics. Faster cooling, by for example injection moulding, can therefore improve the ductility of pCBT. However, non-isothermal processing is not considered to be an option for RTM since it would increase the cycle times significantly.

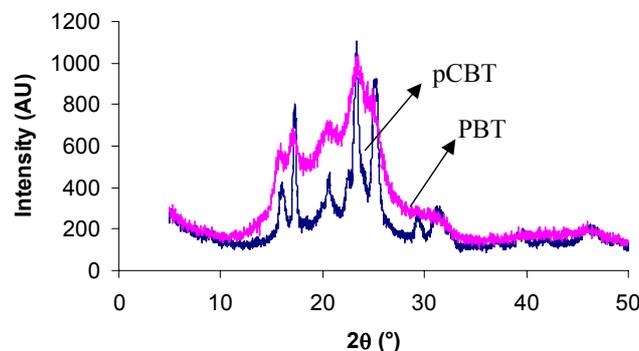


Fig. 2 WAXD pattern of pCBT and PBT

The crystalline structure was further investigated by X-ray diffraction and TEM. Fig. 2 shows the WAXD pattern of pCBT and PBT. There was no significant difference between pCBT processed at 190 and 230 °C. There is however a substantial difference between PBT and pCBT. Although both samples clearly exhibit an α -phase structure [6], PBT shows very broad peaks (small imperfect crystals) superimposed on a clear amorphous halo whereas pCBT closely resembles a perfect crystal, with a very small amorphous halo. Since the diffraction patterns were recorded in reflection mode, part of the more crystalline core of the injection-moulded samples may be lacking from these patterns.

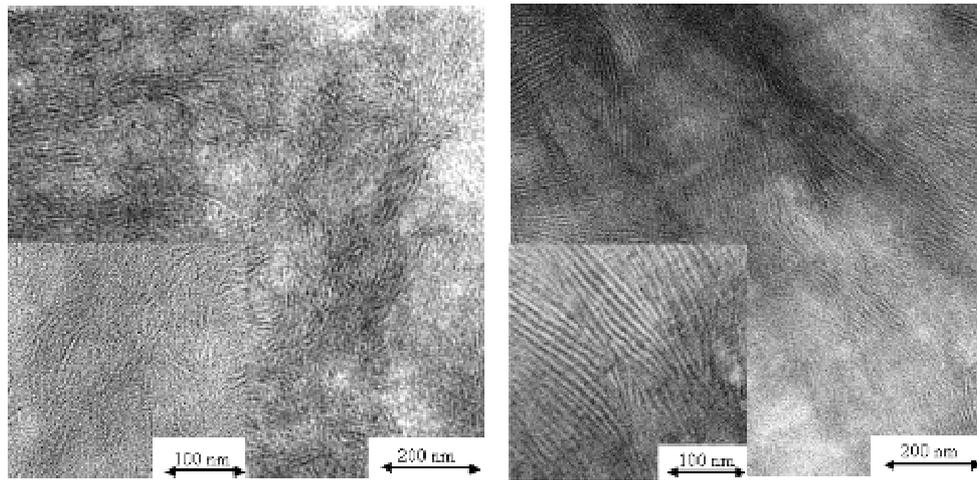


Fig. 3 TEM micrographs (left) PBT (right) pCBT

Fig. 3 shows the TEM micrographs of both PBT and pCBT. In contrast to the PBT sample, the lamellae in the pCBT samples are well defined, thicker and nicely oriented. From these micrographs and the WAXD pattern, it is clear that these pCBT crystals have a higher degree of perfection compared to fast crystallised PBT. Even when polymerised above the melting point and consecutively slow crystallised, imperfections are not induced. This too perfect crystal structure together with a lower density of tie molecules, as indicated by the clear contrast between the crystalline and amorphous phase, is very likely to be responsible for the brittleness of pCBT.

3.3 Reprocessing of pCBT and PBT

From the results presented above, it is clear that pCBT is brittle when processed under similar conditions as it would be in RTM. In order to investigate the intrinsic ability of pCBT to behave like a ductile material, both pCBT and PBT were grinded and reprocessed by injection moulding (giving RP-PBT and RP-pCBT). The resulting tensile bars were tested and the broken specimens are shown in Fig. 4. Even though it is obvious that the RP-PBT shows more necking than the RP-pCBT, some of the latter samples clearly show neck formation and thus ductile behaviour.



Fig. 4 Tensile samples after testing (left) RP-PBT (right) RP-pCBT

Table 4 shows the properties of the reprocessed specimens as well as some properties of injection moulded CBT resin (IM-CBT), polymerised during moulding and with a lower catalyst level (0.33 wt% versus 0.45 wt%). The modulus of RP-pCBT decreased in comparison with pCBT but is now quite similar to both PBT and RP-PBT as is the yield strength.

Table 4 Properties of RP-pCBT, RP-PBT compared to injection-moulded pCBT

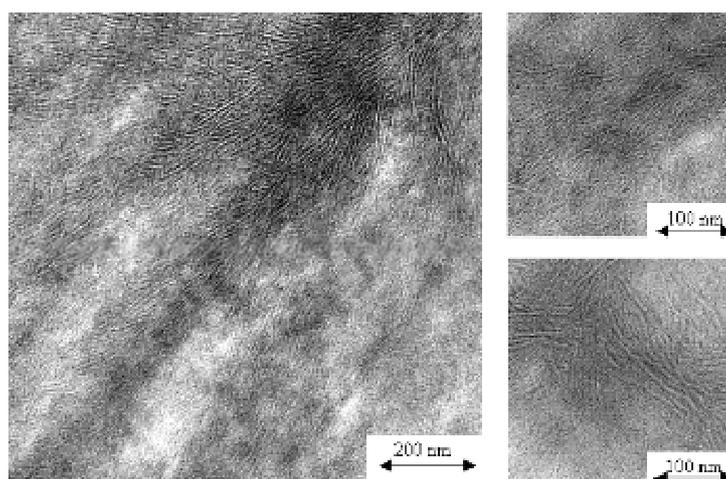
	E (MPa)	σ^* (MPa)	ε^* (MPa)	M_n (kg/mol)	M_w (kg/mol)	α (%)	χ_c (%)
RP-pCBT	2.3 ± 0.2	46 ± 7	170 ± 137	20.5 ± 1.9	40.6 ± 4.3	97.9 ± 0.1	30 ± 1
RP-PBT	2.5 ± 0.2	50 ± 1	16 ± 10	32.3 ± 0.2	66.3 ± 0.5	98.7 ± 0.1	22 ± 1
IM-pCBT^a	2.4	55	160	/	113	/	/

^a Data from injection moulded tensile bars of CBT polymerised during moulding, 0.33 wt% of catalyst, [9, 10]

The GPC-measurements revealed a large drop in molecular weight for the RP-pCBT compared to the pCBT, which is not as pronounced in RP-PBT. Hydrolysis of PBT in the presence of water is known to decrease the molecular weight and although the samples were dried before reprocessing, the catalyst still present in the pCBT samples might have a negative effect on this degradation reaction.

The resulting molecular weight of the RP-pCBT is lower than the critical molecular weight for molecular entanglement mentioned above. This limit was however deduced from previous tests of PBT with varying molecular weights [13] and must therefore not be seen as absolute. It is however clear that the molecular weight of the RP-pCBT is close to the critical molecular weight, therefore, not all specimens show necking. When the molecular weight of pCBT is however large enough after injection moulding, ductile behaviour comparable to that of PBT is observed, Table 4.

The WAXD pattern of the RP-pCBT resembles the original pattern of PBT shown in Fig. 2, indicating a similar degree of crystal perfection and size. The TEM micrographs on the other hand revealed a non-homogeneous structure, Fig. 5. Although a structure very similar to PBT is present, some parts clearly exhibit better-defined, oriented and wider lamellae.

**Fig. 5** TEM micrograph of RP-pCBT

Even though the pCBT was grinded and molten before injection moulding, some of its original structure was restored upon recrystallisation, indicating lack of molecular entanglement probably due to insufficient homogenisation at molecular level. Together with the slow cooling rate, this might help to understand why under stagnant conditions CBT

polymerised above the melting point of PBT still crystallises as if it was simultaneously polymerised, that is because of the lack of molecular entanglement.

4 CONCLUSIONS

Infusing low viscous thermoplastic prepolymers into a fibre preform to produce textile reinforced thermoplastics seems to be very promising since it combines both the advantages of thermoplastics and the ease of impregnation of thermoset resins. The mechanical properties of the glass fibre reinforced polymerised cyclic butylene terephthalate however indicated that polybutylene terephthalate, resulting from isothermal and simultaneous polymerisation and crystallisation, behaved like a brittle matrix.

The production route of CBT[®] resins in a RTM like process gives rise to well-defined, thick and well-oriented lamellae. Together with a low density of tie molecules, these large and perfect crystals cause polymer brittleness. When polymerisation and crystallisation were consecutive under stagnant conditions and the cooling rate was low, similar crystal perfection was obtained. Reprocessing of the brittle polymer partially destroys the crystal structure resulting in a more ductile material. If CBT[®] resins are crystallised from a truly random melt at a sufficiently high cooling rate, they will behave as classical injection moulded PBT.

Since non-isothermal processing would substantially increase the cycle time in RTM, it is not an option for this production route for composites to rapidly cool down the matrix from the melt, even though this would increase ductility. For the RTM process, it is therefore necessary to destroy the too perfect crystal structure by chemically introducing imperfections like for example branching.

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