Thermoplastic Liquid Composite Molding: Production and Characterization of Composites Based On Cyclic Oligomers

Hilde Parton [1], Ignaas Verpoest [1]

[1] *Department of Metallurgy and Materials Engineering, K.U.Leuven*
Kasteelpark Arenberg 44, B-3001 Leuven, BELGIUM
Corresponding Author's e-mail: hilde.parton@mtm.kuleuven.ac.be

SUMMARY: The use of low viscous polymeric precursors like cyclic butylene therephthalate oligomers, which can react to form a thermoplastic matrix, allows thermoset production techniques such as resin transfer molding to be used for the production of continuously reinforced thermoplastic composites. Given that the matrix is polymerized inside a closed mold and in the presence of fibers, the relation between the matrix and composite properties has been studied for different preforms. In order to assess the experimental data, the composite properties were predicted with the classical laminate theory. Although most fibers and more specifically their sizing do not completely inhibit polymerization, some do lead to inferior matrix properties which affect the non-fiber dominated composite properties. In order to assess the feasibility of producing large parts with this production technique, a thermoplastic leaf spring prototype was manufactured. Even though some optimization is still required to improve process reproducibility, the resulting product quality was satisfactory. Moreover, most of the problems occurring during processing are inherent to the RTM process and not related to the matrix system.

KEYWORDS: thermoplastic, RTM, cyclic oligomers

INTRODUCTION

The main problem during the processing of thermoplastic composites is the impregnation of the fibrous reinforcement with highly viscous resins. Therefore, liquid composite molding techniques are typically associated with thermoset resins. Recently, however, more attention has been paid to in situ polymerization techniques, where impregnation is facilitated by injecting polymeric precursors, which then react to form a thermoplastic matrix. The low viscosity of these precursors allows for the use of liquid molding techniques like resin transfer molding for the production of continuously reinforced thermoplastics.

This paper reports on the characterization of continuously reinforced thermoplastics made by RTM as well as the production of a thermoplastic leaf spring prototype.

PRODUCTION AND CHARACTERIZATION OF A4-SIZED PLATES

Materials

The prepolymers used in this study were the cyclic butylene therephthalate oligomers (CBT® resin) supplied by Cyclics Corporation. These oligomers are precursors for the thermoplastic polybutylene therephthalate (PBT). The number of butylgroups 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 polymerization reaction. The tin-based catalyst (Fascat™ 4101) is commercially available from Atofina Chemicals Incorporated.

Four types of glass fiber reinforcements were used, which were all dried overnight at 110 °C before processing. These reinforcements were used to produce composites of 2 mm thickness. The first fabric (S-UD) supplied by Saertex Wagener GmbH, is a non-crimp unidirectional fabric with a total areal density of 951 g/m². Although this fabric is mostly unidirectional, a small amount of 90° fibers (27 g/m²) was added to ensure for fabric stability. Three layers of this fabric were used, resulting in a total fiber volume fraction of 54 %. A biaxial (± 45°), non-crimp fabric (S-B) from Saertex was also used. The measured areal density of the fabric is 590 g/m². Four layers were used to reach a fiber volume fraction of 46 %.

Ahlström Fiber Composites supplied a second type of non-crimp fabric, which consists out of three layers, 0°, 90° and a random mat. The areal density of these individual layers was determined experimentally resulting in respectively 1217, 60 and 53 g/m². Two layers of these fabric were used $(0, R, 90)_s$ to reach a fiber volume fraction of 52 %.

Eurocarbon B.V. developed a braid for a leaf spring prototype. Each layer of this braid consists for 84 % out of 0° fibers, whereas the ± 45° fibers only encompass 16 % of the total areal weight, which is 1200 g/m². Two layers of this fabric were used, resulting in a total fiber volume fraction of 48 %. The unidirectional fibers are not of the same type as the ± 45° fibers. In order to use this braid into the plate mold, the braid was cut open.
PBT Twintex from Vetrotex Renforcement S.A., which is a 2 × 2 twill weave, was used as a reference material. The areal density is 1030 g/m² with a fiber weight fraction of 65 % in 2.5 mm thick composite.

Production of flat plates

The production of glass fiber reinforced polymerized 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 mold, containing the fibrous reinforcement. During this stirring time, polymerization already commences, resulting in a continuously increasing viscosity and thus a limited time window for mold filling. Once the mold is completely filled, in- and outlet ports are closed after which sufficient time (30 min) should be available to complete the polymerization reaction and cold crystallization.

Characterization of pCBT

The characterization methods used for the determination of the matrix properties, which are described in detail elsewhere [1], include gel permeation chromatography (GPC) en differential scanning calorimetry (DSC).

Fig. 1 shows the GPC results for different pCBT composites. It is clear that both the degree of conversion and the molecular weight decrease when fibers are present during polymerization. It was previously demonstrated that the degree of conversion is underestimated by a few percent for the fiber reinforced pCBT [1], therefore, the remaining oligomer content for most composites is satisfactory. Although ECA-UD has an oligomer content of less than 10 %, visual observation of the composites revealed fiber-matrix incompatibility. In the vicinity of the fibers, the matrix was yellowish, compared to bright white for unreinforced pCBT. This color difference also translates in the lowest measured molecular weight.

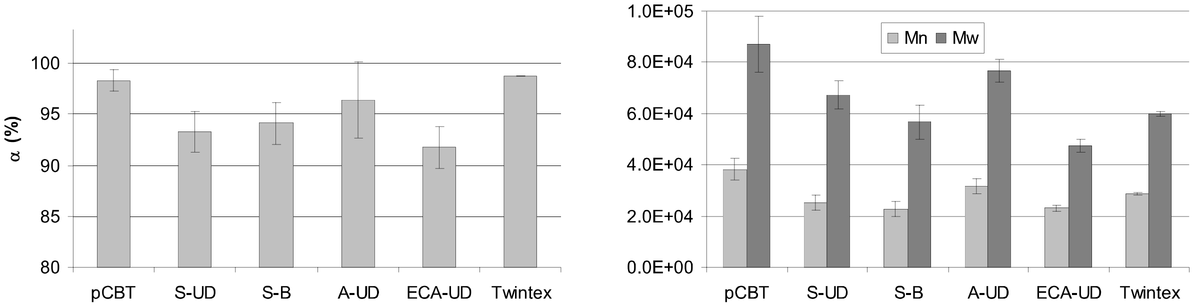

Fig. 1 GPC results

The degree of crystallinity was determined by DSC measurements, Fig. 2. There is no major difference between the unreinforced and reinforced pCBT. Compression molded Twintex-PBT has however a significantly lower degree of crystallinity. PBT is usually crystallized from the melt, as is the case for the Twintex PBT. pCBT on the other hand can start crystallization before polymerization is fully completed, resulting in a different degree of crystallinity, depending on the polymerization temperature and a different crystalline structure. The difference in crystalline structure strongly influences the matrix toughness, but will not be further discussed here [2].

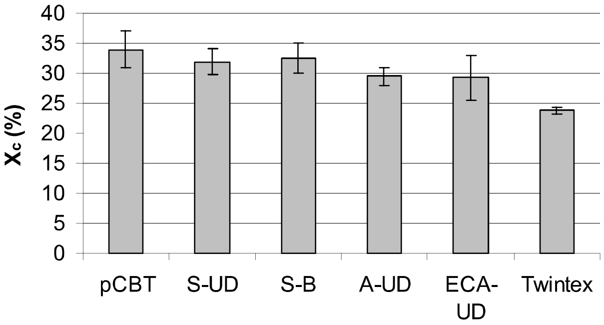

Fig. 2 Degree of crystallinity

Mechanical properties

The mechanical properties of the composites 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. The transverse unidirectional properties were calculated with both the equations of Chamis and those of Thai-Hahn ($\eta = 0.5$) [3].
Both the experimental and theoretical moduli are shown in Fig. 3. The longitudinal modulus is a fiber dominated property and should therefore not be affected by poor matrix polymerization. The somewhat larger discrepancy for the ECA-UD samples can be explained by a deviation of the fiber orientation due to the nature of the fabric (cut-open braid).

The transverse modulus is on the other hand a matrix- and interface dominated property. Although it is known that predicting the non-fiber dominated properties is less accurate, the deviation of almost 50 % for the ECA-UD samples clearly indicates inferior matrix properties, which was confirmed by the GPC results, which show the lowest degree of conversion and the lowest molecular weight for the ECA-UD matrix.

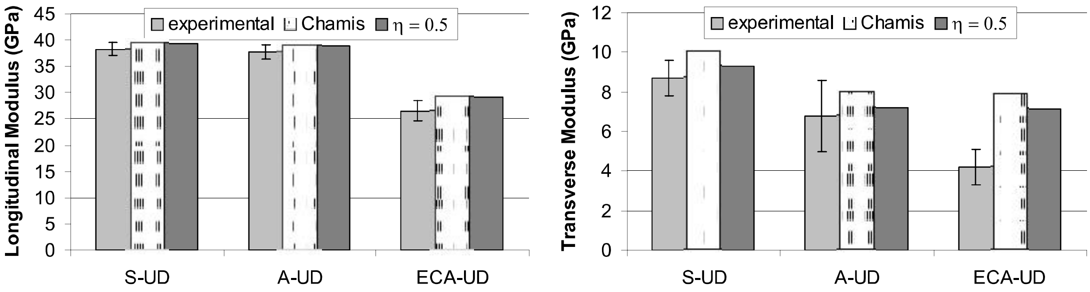

Fig. 3 Mechanical properties compared to theoretical predictions

LEAF SPRING PROTOTYPE

Materials

The braided preform for the leaf spring consisted out of 6 layers of braiding (ECA-UD), braided over a metal template, which was removed after the braiding process. Unfortunately, the template was a little bit too wide, resulting in difficulties in placing the preform into the mold cavity. The total weight of the leaf spring preform was 2.1 kg.

Two matrix materials were used, namely CBT® resin, which was described above and for comparative reasons, an epoxy resin Epikote 828 with curing agent Epicure DX-6514 was also used to produce two prototypes.

Production of thermoplastic leaf springs

In order to enlarge the time window for fiber impregnation with the reactive mixture, the oligomer melt (2 kg) was kept at 170 °C as compared to 190 °C for the production of the flat plates. Lowering the temperature of the oligomer-catalyst mixture, decreases the reaction speed and thus the viscosity of the entering liquid. In order to complete polymerization in a reasonable timeframe and to optimize the matrix properties, the mold temperature was still kept at 190 °C. Stirring time for the catalyst/oligomer mixture was 45 s. The resin mixture was injected into the mold with an overpressure of maximum 2.5 bar and assisted by an underpressure of 0.8 bar. Fig. 4 shows the set-up for the production of the thermoplastic leaf spring. In order to enhance mold filling, an injection channel along the length of the leaf spring was foreseen.

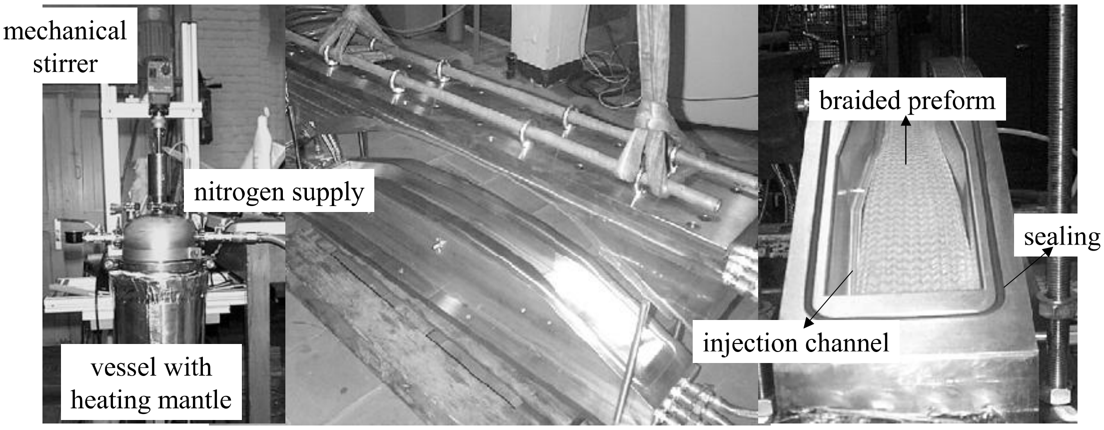

Fig. 4 Set-up for production of leaf spring

Table 1 gives an overview of the processing parameters and filling times needed to produce the leaf spring prototypes. For the production of the leaf springs, there were two major parameters changed, namely the position of the mold and the filling of the distribution channel. The mold was rotated in order to enhance air evacuation by placing the vents at the highest point. The distribution channel was filled with roving and or partially closed with sealing in order to on one hand slow down the resin flow inside the channel and on the other hand to avoid short cut flows due to imperfect fitting of the preform.

Table 1 Processing parameters for leaf spring production

	Epoxy 1	**Epoxy 2**	**pCBT 1**	**pCBT 2**	**pCBT 3**	**pCBT 4**	**pCBT 5**	**pCBT 6**
mold rotation	0°	0°	0°	180°	180°	180°	90°	90°
distribution channel	empty	empty	empty	roving	roving	roving	roving+ sealing	roving + sealing
overflow time	75	90	60	120	100	N.A.	90	N.A.
filling time	600	900	300	300	300	375	420	270

From the production of these prototypes, it became clear that the process is not yet very reproducible. Both the time to reach the first overflow and the time to reach air-free overflow (filling time) changes although other parameters are kept constant. There was no major difference in the irreproducibility between the very low viscous oligomers and the epoxy resin. Even though there are a number of factors that have to be taken into account, such as the pressure profile, the fiber preform plays a major role.

The preform was braided around a mandrel with the inner section of the mandrel being 60 mm wide. This leads to a preform width of around 70 mm, which is substantially larger than the 66.5 mm of the actual leaf spring. Compression of the braid to fit into the mold cavity causes the transverse permeability to decrease 22 %, calculated with the formulas of Gebart [4]. The amount of prefrom compression changed from one production run to another. Sometimes fibers from the outer braid were trapped inside the injection line and/or distribution channel, therefore altering the transverse permeability and thus causing process irreproducibility.

Another effect of the need to compress the fiber preform in the middle section, is the impossibility to closely fit the preform to the mold cavity in the widening region of the leaf spring. This leads to gaps exceeding 3 mm between the fiber preform and the mold cavity. In combination with a non-perfect fit of the preform at the outer sides of the leaf spring, short cut flows are almost unavoidable. These short cut flows are responsible for the sometimes very sudden overflow. It is therefore crucial to produce a preform, which fits perfectly inside the mold cavity without major handling.

The time for this resin-catalyst combination to complete polymerization and crystallization is only 30 minutes, which, in an automated process, can be the total cycle time, since the mold does not need to cool down before demolding. For this prototype set-up however, a minimum cycle time of 3 hours was needed due to thermal cycling of the mold, preform preparation excluded. The prototype is shown in Fig. 5 and weighed 2.9 kg after proper trimming.

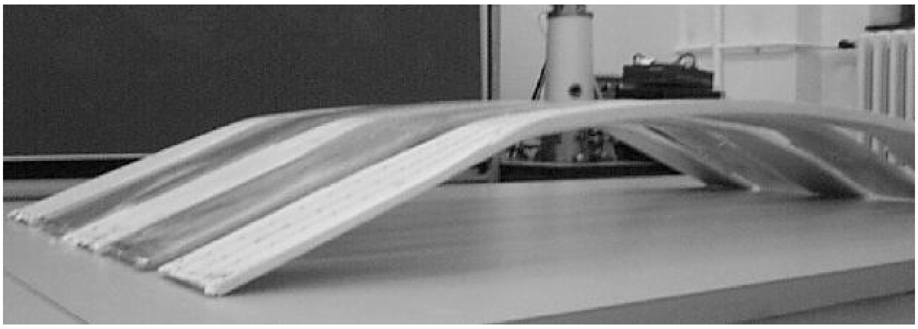

Fig. 5 Leaf spring prototypes

Testing of leaf spring prototype

The leaf spring prototypes were tested in four point bending mode as shown in Fig. 6. A maximum load of 10 kN was obtained, which corresponds to a roller displacement of 250 mm. At this large displacement, strain in the outer fiber was only 2 %. A short-term cyclic loading was also applied, leading to a constant spring constant of 30 N/mm.

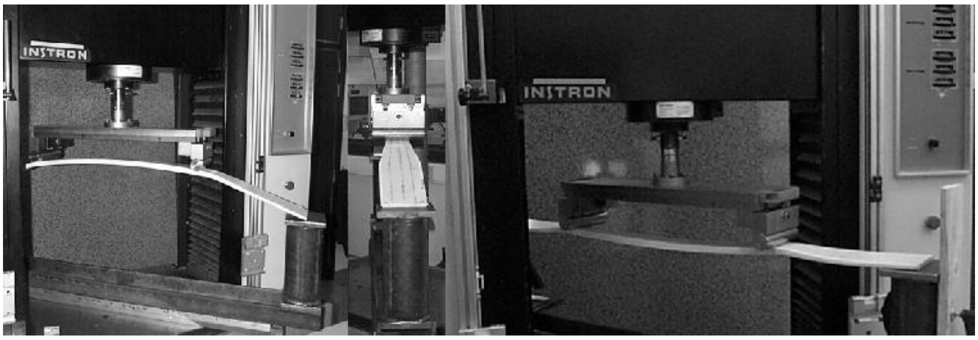

Fig. 6 Testing of leaf spring prototype

CONCLUSIONS

Liquid molding technologies were used to manufacture continuously reinforced themoplastic composites by utilizing polymeric precursors that were polymerized in situ. Although most fibers and more specifically their sizing do not completely inhibit polymerization, some do lead to inferior matrix properties which affect the non-fiber dominated composite properties such as the transverse modulus in unidirectional composites.

Scaling-up the process was assessed by the production of a thermoplastic leaf spring prototype. Although optimization of the braided preform is necessary to improve process reproducibility, the encountered problems were inherent to the RTM process and not related to the resin system. The final product quality and mechanical properties were satisfactory.

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